EDIBLE FATS AND OILS

W. H. SIMMONS AND C. A. MITCHELL

SECOND REVISED EDITION

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EDIBLE FATS AND OILS

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EDIBLE FATS AND OILS

THEIR COMPOSITION, MANUFACTURE AND ANALYSIS

BY

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PREFACE TO SECOND EDITION

This work was originally planned by Mr. Simmons, and was intended to afford general information upon the preparation, properties and meaning of the analytical characters of oils and fats. It was not meant to replace the larger text-books on the subject, but rather to enable chemists with only a slight knowledge of the chemistry of oils and fats to apply the tests most commonly used, and to interpret their analyses, at all events in the more simple cases.

Unfortunately, owing to illness, Mr. Simmons was obliged to abandon any active part in the work, which was therefore finished by the writer. It is necessary to mention these facts, because, whilst the first edition might be regarded as the joint work of two authors, the writer is solely responsible for the additions to the present edition.

These additions include an extension of the chapter on margarine, and a new chapter dealing with hydrogenated oils, both of which will, it is hoped, add to the usefulness of the book. A summary has also been given of recent work on the so-called vitamines.

C. A. M.

London,
February, 1921.

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EDIBLE FATS AND OILS

CHAPTER I

INTRODUCTION

Fat as Food—Physiological Considerations—Vitamines—Constitution of Fats and Oils—Analytical Values or Constants.

THE food of man may be divided broadly into two classes, *nitrogenous*, or flesh-forming, which is mainly of animal origin, and *carbonaceous*, or energy-producing, derived both from the animal and vegetable kingdoms. Besides nitrogen and carbon, many other elements, of course, such as phosphorus, calcium, iron, etc., normally enter into the composition of human food, but the nitrogen and carbon constitute the chief ingredients thereof, and are absolutely necessary to maintain the body in a healthy and efficient state.

There is an almost infinite variety of forms in which carbon may be taken into the stomach, but the vast majority of carbonaceous foods may be classified in two great chemical families: (1) the *carbohydrates*, comprising starch, sugar, and similar substances, which consist of carbon, hydrogen, and oxygen, the two latter in quantities having the same ratio as in water; and (2) the *oils and fats*, with which in the present volume it is proposed to deal.

Physiological Considerations.—The primary function of carbon-containing food is, by its combustion, to produce heat or other form of energy. The combustion of 1 gram of carbon to carbon dioxide produces 8080 calories; of 1 gram of hydrogen to water, 34,462 calories; whilst the presence of oxygen actually reduces the calorific value of the substance. Hence the higher the proportion of carbon, and lower the amount of oxygen, the greater will be the heat-producing power of a food; and since fats are much richer in carbon than starch or sugar, containing about 2½ times as much, they constitute the most concentrated form in which fuel can be supplied to the body. In the case of animal fats, carbon in the form of carbohydrate is converted into fat by the animal organism, and is thus rendered more suitable for the food of man; as although man in his internal economy, principally by means of his liver, is quite capable of himself transforming starchy matter into fat, in so doing he expends a certain amount of energy. Moreover, the human stomach is relatively smaller than that of an animal, and therefore a more highly concentrated form of carbon-containing food is desirable. Dripping is especially rich in carbon, containing over 10 per cent. more than does butter or suet, and it is regrettable that the use of dripping, formerly so popular among the working classes, has now become so largely a thing of the past.

The average relative proportions of fat and carbohydrate in the food of man vary with the climate, and are also governed to a considerable extent by their availability. Thus in very hot regions carbohydrates predominate, whilst in colder countries chiefly fat is consumed. The Eskimo takes almost all his carbon in the form of oil and fat, whereas the Indian or Chinese subsists mainly on carbohydrates. In this country the proportions recommended by physiologists, though varying slightly, are about 1 part of fat to 10 parts of carbohydrates, the amount of fat desirable being slightly higher in winter than in summer.

Besides its value as a heat or energy producer, the presence of a proportion of fat in human food is important in other ways, for the "food value" of any substance depends not only upon its composition, but also on its digestibility and palatability; and whilst fats are much more readily assimilated than carbohydrates, they also render more palatable, and assist in the digestion of, other articles of food.

Butter is the most easily digested of all fatty foods, and in cases where a fat diet is necessary, up to $\frac{1}{4}$-lb. of butter can be absorbed per diem. Margarine, which is usually made to approximate fairly closely to butter in composition, except in so far as the butter contains butyric and other volatile fatty acids in larger proportion, should be as digestible as butter, and is almost universally agreed to be so.

Yet another useful purpose served by a proportion of fatty food consists in facilitating the passage of masticated food to the stomach, and of the refuse matter through the bowel.

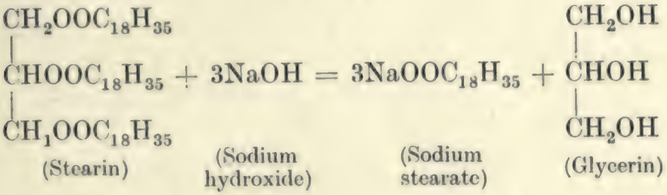
Vitamines.—Certain substances of ill-defined chemical constitution have been shown to be essential for the growth and development of the young and for the maintenance of health in the adult. These substances, which have somewhat inaptly been termed *vitamines*, are widely distributed in vegetable products. Some are soluble in water, and occur to a pronounced extent in vegetables such as onions and in cereals, whilst others are soluble in fats. Vitamines of the latter kind are present in most animal fats (with the curious exception of lard), and for this reason animal fats, such as butter or animal oils, have a growth-stimulating property, which is absent from most vegetable fats or the margarine prepared exclusively from them.

Animals fed upon substances deficient in this factor are much more liable to the attack of bacteria than those whose food contains a proper proportion of vitamines.

The growth-promoting factor in butter fat or whale oil is destroyed by heating the fat for an hour at 100° C., or for a longer time at a somewhat lower temperature.

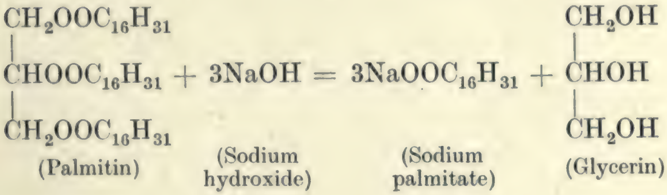
The component of the fat to which the activity is due has not been identified with any of the known constituents, such as the pigment, phosphatic substances, etc.

Constitution of Fats and Oils.—The difference between a fat and an oil is entirely dependent upon temperature, a fat becoming an oil when it is melted, and an oil a fat when solidified. The term *oil* is used for substances differing widely both in composition and properties, but all the fats and oils used for edible purposes are of the same general type of constitution, viz. esters or salts of glycerin with one or more fatty acids, which are termed "glycerides." Their composition was first placed on a scientific basis by Chevreul, who in the early part of the last century showed that when a fat, such as tallow or lard, was converted into soap by the action of sodium or potassium hydroxide, the fat was decomposed into glycerin and fatty acids, the latter combining with the alkali to form the soap, while the glycerin, remaining free, was separated in the lyes. The three glycerides of most frequent occurrence are stearin and palmitin (of which tallow chiefly consists) and olein (the principal constituent of olive oil), and the action of sodium hydroxide on these may be represented by the following equations :—



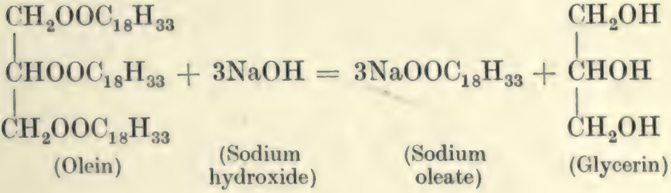
$$\begin{array}{l}CH_2OOC_{18}H_{35}\\ |\\ CHOOC_{18}H_{35}\\ |\\ CH_1OOC_{18}H_{35}\end{array} + 3NaOH = 3NaOOC_{18}H_{35} + \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

(Stearin) (Sodium hydroxide) (Sodium stearate) (Glycerin)



$$\begin{array}{l}CH_2OOC_{16}H_{31}\\ |\\ CHOOC_{16}H_{31}\\ |\\ CH_2OOC_{16}H_{31}\end{array} + 3NaOH = 3NaOOC_{16}H_{31} + \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

(Palmitin) (Sodium hydroxide) (Sodium palmitate) (Glycerin)



$$\begin{array}{l}CH_2OOC_{18}H_{33}\\ |\\ CHOOC_{18}H_{33}\\ |\\ CH_2OOC_{18}H_{33}\end{array} + 3NaOH = 3NaOOC_{18}H_{33} + \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

(Olein) (Sodium hydroxide) (Sodium oleate) (Glycerin)

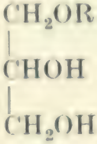
The conclusions of Chevreul as to the composition of fats were subsequently confirmed by Berthelot, who succeeded in producing the glycerides synthetically by heating the fatty acids with glycerin under pressure in sealed tubes. Heating together, for example, stearic acid and glycerin, he obtained stearin, according to the equation :—

$$3C_{18}H_{35}O_2H + C_3H_5(OH)_3 = C_3H_5(C_{18}H_{35}O_2)_3$$

In view of the fact that glycerin contains three hydroxyl (OH) groups in which the H is displaceable by an acid radicle, it follows that compounds may be formed, in which only one, or two, or all three of the hydrogen atoms are replaced by an acid, compounds of the following types resulting; where R represents a fatty acid radicle.

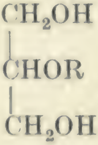
Monoglyceride :—

(Alpha)



$$\begin{array}{l}CH_2OR\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

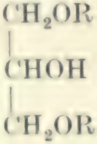
and (Beta)



$$\begin{array}{l}CH_2OH\\ |\\ CHOR\\ |\\ CH_2OH\end{array}$$

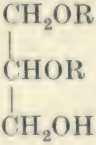
Diglyceride :—

(Alpha)



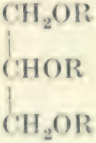
$$\begin{array}{l}CH_2OR\\ |\\ CHOH\\ |\\ CH_2OR\end{array}$$

and (Beta)



$$\begin{array}{l}CH_2OR\\ |\\ CHOR\\ |\\ CH_2OH\end{array}$$

Triglyceride :—



$$\begin{array}{l}CH_2OR\\ |\\ CHOR\\ |\\ CH_2OR\end{array}$$

Intermediate products, corresponding with the above formulæ for the mono- and di-glycerides, were obtained by Berthelot in his syntheses, but in fresh natural oils and fats glycerides are only met with in which all the hydrogen atoms in the hydroxyl groups are displaced by an acid.

Formerly it was believed that in nature the acid radicles combining with the same molecule of glycerin were all identical, but during the last few years a large number of so-called "mixed glycerides" have been discovered in various oils and fats, which may be represented by the above formula for the triglyceride, if the radicles denoted by R are assumed to be not all alike. Among these mixed glycerides may be mentioned oleodipalmitin, $C_3H_5(OC_{18}H_3O)$ $(OC_{16}H_{31}O)_2$; stearodipalmitin, $C_3H_5(OC_{18}H_{35}O)$ $(OC_{16}H_{31}O)_2$; oleopalmitostearin, $C_3H_5(OC_{18}H_{33}O)$ $(OC_{16}H_{31}O)$ $(OC_{18}H_{35}O)$; and palmitodistearin, C_3H_5 $(OC_{16}H_{31}O)$ $(OC_{18}H_{35}O)_2$ obtained by Hansen, and by Bömer from tallow; stearodipalmitin being also found in goose and turkey fat by Klimont and Meisels, and palmitodistearin in lard by Kreis and Hafner.

Mixed glycerides containing highly unsaturated fatty acids have been isolated from fish oils, and it is probable that the butyric acid present in butter fat exists as a mixed glyceride, and not as butyrin; indeed, mixed glycerides are claimed to have been found in butter fat by Bell, and Blyth, and Harrison respectively.

It is a remarkable fact that the fatty acids occurring in natural oils and fats appear always to contain an even number of carbon atoms. Although fatty acids, such as *margaric acid*, $C_{17}H_{34}O_2$, have been made synthetically, their alleged occurrence in olive oil and palm oil has not been confirmed, and the preparations isolated by Holde and Stange have been shown to be composed of mixtures of fatty acids containing an even number of carbon atoms.

The following are the chief pure triglycerides, together with their source, formulæ, and more important constants :—

Glyceride.	Formula.	Chief Occurrence.	Melting point, °C.	Refractive Index, at 60° C.	Saponification Equivalent.
Butyrin.	$C_3H_5(OC_4H_7O)_3$	Butter fat.	Liquid at −60	1·42015	100·7
Isovalerin.	$C_3H_5(OC_5H_9O)_3$	Porpoise, dolphin and whale oils.	...	...	114·7
Caproin.	$C_3H_5(OC_6H_{11}O)_3$	Coconut and palm-nut oils.	−25	1·42715	128·7
Caprylin.	$C_3H_5(OC_8H_{15}O)_3$	Coconut and palm-nut oils.	−8·3	1·43316	156·7
Caprin.	$C_3H_5(OC_{10}H_{19}O)_3$	Coconut and palm-nut oils.	31·1	1·43697	184·7
Laurin.	$C_3H_5(OC_{12}H_{23}O)_3$	Coconut and palm-nut oils.	45	1·44039	212·7
Myristin.	$C_3H_5(OC_{14}H_{27}O)_3$	Nutmeg butter, Butter fat.	56·5	1·44285	240·7
Palmitin.	$C_3H_5(OC_{16}H_{31}O)_3$	Palm oil, lard.	63–64	...	268·7
Stearin.	$C_3H_5(OC_{18}H_{35}O)_3$	Tallow, lard, cacao butter.	71·6	...	296·7
Olein.	$C_3H_5(OC_{18}H_{33}O)_3$	Olive and almond oils.	Solidifies at −6	...	294·7
Ricinolein.	$C_3H_5(OC_{18}H_{33}O_2)_3$	Castor oil.	...	...	310·7

It will be observed that butyrin and olein are both liquid at ordinary temperatures, whilst stearin and palmitin have comparatively high melting points. Fats such as tallow or palm oil, therefore, in which the proportion of these latter is high, are firm and hard, the degree of hardness increasing with the percentage of these glycerides.

Butyrin (Tributyrin) may be obtained by heating together butyric acid and glycerin under pressure. According to Scheij its specific gravity is $d\frac{20°}{4°} = 1{\cdot}0324$, and $d\frac{60°}{4°} = 0{\cdot}9963$. It is almost insoluble in water, and has an intensely bitter taste.

Laurin (Trilaurin) may be produced by heating together lauric acid and glycerin. It is readily soluble in ether, but only slightly so in cold absolute alcohol, and crystallises in needles, melting at 45–46° C., and having, according to Scheij, the specific gravity $d\frac{60°}{4°} = 0{\cdot}8944$.

Myristin (Trimyristin) may be isolated from nutmeg butter by fractional distillation *in vacuo*, or can be prepared by heating together myristic acid and glycerin. It crystallises in laminæ, which on heating first melt at 56·5° C., but again solidify, as the temperature is further raised, at 57–58° C. The product then has a melting point of 45–55° C. Its boiling point *in vacuo* is 290–300°, and its density $d\frac{60°}{4°} = 0{\cdot}8848$.

Palmitin (Tripalmitin) may be prepared, artificially by heating together palmitic acid and glycerin, repeatedly boiling the product with alcohol, and allowing it to crystallise, when greasy scales are obtained, having a peculiar pearly appearance. The effect of heat on palmitin is somewhat curious, indicating the existence of distinct modifications. Thus when heated to 46° C. it liquefies, but again becomes solid on further raising the temperature, melting once more at 61·7° C., and becoming cloudy, with separation of crystalline particles. Further increase of temperature to 63° C. renders the liquid clear, and this temperature is regarded as the true melting point. After melting and re-solidifying, palmitin possesses no crystalline fracture.

Stearin (Tristearin) may be separated from tallow by dissolving it in ether and allowing it to crystallise, when small crystals separate, having a bright pearly lustre. Stearin when heated also shows the existence of two modifications. Thus, on raising the temperature to 55° C., stearin liquefies, but again becomes solid on further increasing the temperature until 71·6° C. is reached, when it again melts. If this liquid is further heated to 76° C., and then allowed to cool, solidification does not take place until the temperature has fallen to 55° C., but if, after attaining 71·6°, it is immediately cooled, it will solidify at 70° C.

Olein (Triolein) is one of the most widely distributed natural glycerides, and may be prepared in an impure form from olive oil by separating the solid glycerides by cooling. After maintaining the oil at a low temperature for several days, and separating the liquid portion, the latter may be freed from traces of stearin and palmitin by solution in alcohol. Olein may also be produced artificially by heating together oleic acid and glycerin. It is an odourless, colourless, and tasteless oil, which may be distilled *in vacuo*, without decomposition, but which rapidly absorbs oxygen from the air and becomes rancid.

As already stated, the natural glycerides of which edible fats and oils are composed, consist of combinations of glycerin with various fatty acids. These may be separated by saponifying the fat or oil with sodium or potassium hydroxide, dissolving the resulting soap in hot water, and adding sufficient dilute sulphuric acid to decompose the soap, when an oily layer gradually rises to the surface. This when melted by gentle heat and washed free from mineral acid, is soluble in alcohol and reddens blue litmus paper. It consists of the insoluble fatty acids of the fat, those soluble in water, such as acetic, propionic, butyric, caproic, caprylic, and capric acids, remaining for the most part dissolved in the aqueous portion underneath.

All the acids naturally present in fats and oils are monobasic, *i.e.* contain only one carboxyl (COOH) group, but they may be arranged in six classes or homologous series, based on their chemical constitution, these series having the following general formulæ :—

I.	Stearic Acid Series	$C_nH_{2n+1}COOH$.
II.	Oleic Acid Series	$C_nH_{2n-1}COOH$.
III.	Linolic Acid Series	$C_nH_{2n-3}COOH$.
IV.	Linolenic Acid Series	$C_nH_{2n-5}COOH$.
V.	Clupanodonic Acid Series	$C_nH_{2n-7}COOH$.
VI.	Ricinoleic Acid Series	$C_nH_{2n-2}(OH)COOH$.

The more important members of these series, together with their formulæ, melting points, and principal sources, are given in the following tables :—

I. Stearic Series

Acid.	Formula.	Melting point, °C.	Found in—
Acetic.	CH_3COOH	17	Macassar oil.
Butyric.	C_3H_7COOH	...	Butter, macassar oil.
Isovaleric.	C_4H_9COOH	...	Porpoise and dolphin oils.
Caproic.	$C_5H_{11}COOH$	...	Butter, coconut oil.
Caprylic	$C_7H_{15}COOH$	15	Butter, coconut oil, Limburg cheese.
Capric.	$C_9H_{19}COOH$	30	Butter, coconut oil.
Lauric.	$C_{11}H_{23}COOH$	44	Coconut oil, palm kernel oil.
Myristic.	$C_{13}H_{27}COOH$	54	Nutmeg butter, liver fat, coconut oil, dika fat, croton oil.
Palmitic.	$C_{15}H_{31}COOH$	62·5	Palm oil, most animal fats.
Stearic.	$C_{17}H_{35}COOH$	69	Tallow, lard, most solid animal fats.
Arachidic.	$C_{19}H_{39}COOH$	75	Arachis or earth-nut oil, rape and mustard-seed oils.
Behenic.	$C_{21}H_{43}COOH$	...	Ben oil, black mustard-seed oil, rape oil.
Lignoceric.	$C_{23}H_{47}COOH$	80·5	Arachis oil.
Carnaubic.	$C_{23}H_{47}COOH$	...	Carnauba wax.
Hyænic.	$C_{24}H_{49}COOH$	...	Hyæna fat. (?)
Cerotic.	$C_{25}H_{51}COOH$	78	Beeswax, spermaceti.
Melissic	$C_{29}H_{59}COOH$	89	Beeswax.

The acids of this series are all what is termed "saturated compounds," *i. e.* they do not form addition compounds when brought in contact with bromine, iodine, or ozone. The two first are liquid at ordinary temperatures, distil unchanged under atmospheric pressure, and are miscible with water in all proportions. The next four are more or less soluble in water, and readily distil with steam, as does also lauric acid, though the latter is practically insoluble in cold water, and only dissolves very slightly in boiling water. These first seven acids are termed *Volatile Fatty Acids*, and on their volatility are based the Reichert process and its modifications and the Polenske method for the examination of butter fat for adulteration, *vide* pp. 143–166. The higher acids of the group are solid, and are completely insoluble in water. All the members of the series are readily soluble in warm alcohol, and undergo no change when heated with solid caustic alkali.

II. Oleic Acid Series

Acid.	Formula.	Melting point, °C.	Found in—
Tiglic.	C_4H_7COOH	64·5	Croton oil.
Moringic.	$C_{11}H_{21}COOH$	...	Ben oil.
Physetoleic.	$C_{15}H_{29}COOH$	30	Sperm oil. (?)
Hypogæic.	$C_{15}H_{29}COOH$	33	Arachis and maize oils.
Oleic.	$C_{17}H_{33}COOH$	14	Most oils and fats.
Rapic.	$C_{17}H_{33}COOH$	...	Rape oil.
Doeglic.	$C_{18}H_{35}COOH$	...	Bottle-nose oil. (?)
Erucic	$C_{21}H_{41}COOH$	34	Mustard oils, marine animal oils, rape oil.

These acids differ essentially from those of Series I. in being unsaturated, and so combine directly with bromine, iodine, and ozone. The earlier members are readily reduced, by the action of sodium amalgam in alkaline solution, to the corresponding acids of Series I. Thus :—

$$\underset{\text{(Tiglic acid)}}{C_4H_7COOH} + \underset{\text{(Hydrogen)}}{H_2} = \underset{\text{(Valeric acid)}}{C_4H_9COOH}$$

This reduction, however, does not take place in the case of the higher acids of the series, and for the reduction of oleic acid to stearic acid other methods have to be adopted.

Acids of this group may also be converted into those of the Stearic Acid Series by heating them to 300° C. with solid potassium hydroxide, when hydrogen is also liberated, the reaction, with oleic acid, for example, being generally represented by the equation :—

$$C_{18}H_{34}O_2 + 2KOH = KC_2H_3O_2 + KC_{16}H_{31}O_2 + H_2$$

though since, as Edmed has shown, a considerable quantity of oxalic acid is also formed, the action must strictly be more complex than this indicates.

One of the most important properties of this group of acids, and one which is of considerable value in judging the purity of olive oil, is the elaidin reaction, which is based on the formation of isomeric acids of higher melting point by these acids when treated with nitrous acid. Oleic acid, for example, when acted upon by nitrous acid, yields elaidic acid, melting at 45° C., and erucic acid gives brassic acid, melting at 60° C. A similar reaction also takes place with the neutral glycerides of these acids, olein being converted into elaidin, which melts at 32° C.

The lead salts of the acids of this series are much more soluble in ether, and the lithium salts more soluble in alcohol, than those of the stearic series, upon both of which properties processes have been based for the separation of the solid from the liquid fatty acids.

III. Linolic Acid Series

Acid.	Formula.	Melting point, °C.	Found in—
Linolic .	$C_{17}H_{31}COOH$	Fluid	Linseed, cotton-seed, and maize oils.
Tariric .	$C_{17}H_{31}COOH$	50·5	Tairiri-seed oil.
Telfairic	$C_{17}H_{31}COOH$	Fluid	Telfairia oil.

These acids are also unsaturated, and readily combine with bromine, iodine, oxygen, or ozone. They do not give an elaidin reaction when treated with nitrous acid, and their lead salts are soluble in ether.

IV. Linolenic Acid Series

Acid.	Formula.	Found in—
Linolenic . .	$C_{17}H_{29}COOH$	Linseed oil.
Isolinolenic . .	$C_{17}H_{29}COOH$	Linseed oil.
Jecoric . .	$C_{17}H_{29}COOH$	Cod-liver and marine animal oils.

These acids are very similar in properties to those of the preceding series, but combine with six atoms of bromine or iodine, whereas the latter only combine with four atoms.

V. Clupanadonic Acid Series

Acid.	Formula.	Found in—
Clupanodonic Acid	$C_{17}H_{27}COOH$	Cod-liver oil, sardine oil.
Unnamed Acid .	$C_{19}H_{31}COOH$	Cod-liver oil, herring oil.

These acids combine with eight atoms of bromine or iodine. They are liquids which rapidly absorb oxygen from the air. Still more unsaturated acids have been isolated from various fish oils.

VI. Ricinoleic Acid Series

Acid.	Formula.	Melting point, °C.	Found in—
Ricinoleic .	$C_{17}H_{32}(OH)COOH$	4–5	Castor oil.

This acid combines with two atoms of bromine or iodine, and when treated with nitrous acid is converted into the isomeric ricinelaidic acid, which melts at 53–53° C. It differs from most fatty acids in possessing optical activity, its specific rotation being $[\alpha]_D = + 6° 25'$.

Alcohols in Fats.—Glycerin or glycerol may be isolated by saponification from the glycerides in oils and fats. In the pure condition it is a colourless oily liquid, which may be obtained in crystals melting at 22° C. It absorbs water rapidly from the air, and, when strongly heated, is decomposed into acrolein and water :—

$$C_3H_8O_3 = 2H_2O + C_3H_4O.$$

Another class of alcohols, which is present in small proportion in oils and fats, includes the crystalline compound *cholesterol* and the isomeric compound *phytosterol*. The former is present in animal fats and the latter in vegetable oils, and their separation and identification (by the crystalline form and melting point) affords a means of distinguishing between animal and vegetable fats.

Analytical Values or Constants.—In the tables of glycerides given in the preceding pages certain distinctive physical and chemical characteristics are assigned to the different individuals. These characteristics are known as the *analytical values* or *constants*, and their determination is a most important point in the analysis of oils and fats, for it frequently affords the means of distinguishing between oils which are otherwise of a very similar character.

Physical Constants.—These include the *melting* and *solidification points* of the fat and of the fatty acids liberated from it, the latter being commonly termed the "titre"; the *specific gravity* compared with water at a definite temperature (usually 15·5° C. for oils); and the *refractive index*, which is most often determined by means of a special instrument known as the *butyro-refractometer*. In certain cases the solubility of the fat in special solvents, such as alcohol or acetic acid, is also determined, whilst in the case of lubricating oils, the *efflux velocity* from a viscosimeter (the viscosity) is an important factor.

Chemical Constants.—The *saponification equivalent* mentioned in the foregoing tables indicates the exact equivalent weight of potassium hydroxide required to convert the fat into a potassium salt and free glycerin. More usually the result is expressed as the *saponification value*, which indicates the amount of potassium hydroxide in milligrams required for the exact saponification of one gram of the oil or fat.

The *Acid Value.*—This is usually not a distinctive characteristic of an oil or fat, since the amount of free fatty acids, which it indicates, largely depends upon the conditions to which the oil has been subjected. Exposure to light and air, the presence of moisture, the action of enzymes in the seed, and the growth of moulds, all have an influence on the decomposition of glycerides into free fatty acids and glycerol. The amount of acid thus liberated is sometimes expressed as a percentage usually of oleic acid, but is more frequently given as the *acid value*, which represents the amount of potassium hydroxide in milligrams required to neutralise the free fatty acids in one gram of the sample.

The *Hehner Value* indicates the percentage of fatty acids insoluble in water and of unsaponifiable matter, separated from an oil or fat by Hehner's process.

The *Reichert-Meissl Value* indicates the proportion of soluble volatile fatty acids, distilled under empirical conditions from five grams of the fat by Meissl's modification of Reichert's process.

The *Polenske Value* represents the proportion of volatile fatty acids insoluble in water separated from an oil or fat under the exact conditions specified by Polenske.

The *Iodine* or *Bromine Value.*—This indicates the percentage of iodine or bromine, or of iodine chloride calculated as bromine, which the oil or fat is capable of absorbing. As pointed out in the following chapter, it affords a means of classifying fats in accordance with their degree of unsaturation.

The *Acetyl Value* represents the amount of potassium hydroxide in milligrams required to neutralise the products formed by the acetylation of an oil with acetic anhydride. It affords a measure not only of hydroxylated acids originally present in an oil (*e.g.* castor oil), but also of free alcohols, oxidised fatty acids and certain compounds formed in the process of rancidity.

Further details of the use of these analytical values in special cases are given in the following pages.

CHAPTER II

RAW MATERIALS USED IN THE MANUFACTURE OF EDIBLE FATS AND OILS

It is unnecessary to emphasise the absolute importance that all materials used for the preparation of edible fats and oils should be as fresh, odourless, and free from all impurities as possible. Albuminous matter, which facilitates the production of rancidity by enzymic action, must be carefully removed, and freedom from any appreciable quantity of free fatty acids is most essential. The absence of these latter should be sufficient to guarantee the absence of any material rancidity, which, though not due to, is generally accompanied by their production.

The general processes of extracting oils and fats, the methods of treatment by which freedom from odour and free fatty acids is secured, are fully described in the next chapter, and in the case of some of the materials, their preparation is dealt with more fully in subsequent chapters. The following paragraphs give briefly the source, origin, and properties of the raw material employed in the industry.

Classification of Oils and Fats.—To facilitate the general survey of the subject, and to afford data for the identification of any particular oil or fat, it is usual to classify these natural products into groups in accordance with their origin, their degree of unsaturation as indicated by their iodine values, or according to the proportion of volatile fatty acids which they contain.

There are thus two main divisions: *Animal* and *Vegetable Fats*, which are subdivided again into *Liquid Fats or Oils* and *Solid Fats*. The vegetable oils are conveniently grouped into the three classes—*non-drying*, *semi-drying*, and *drying oils*, in accordance with their behaviour on exposure in a thin film to the air.

The vegetable fats are classified into those which approximate coconut oil and palm-kernel oil in containing large proportions of volatile soluble and insoluble fatty acids, and *vegetable tallows*, such as cacao butter, characterised by their higher proportion of non-volatile insoluble fatty acids.

Animal Oils, such as neat's-foot oil and the like, are the more fluid fats derived from certain parts of animals, and are distinguished from *marine animal* and *fish oils* by their much lower iodine values, which indicate the presence of fatty acids less highly saturated.

Animal Fats are, in most cases, of the type of lard or of tallow, their consistence largely depending upon the part of the animal from which they were derived. Certain fats of this class, notably those of wild animals, show pronounced drying properties, forming a hard film when exposed to the air in a thin layer.

Butter fat occupies a position in the animal fats analogous to that occupied by coconut oil among the vegetable fats. As in all cases of the classification of natural objects this differentiation is by no means a sharp one, and certain fats might be assigned to different groups according to the property which predominates, whilst others fall on the border line between two classes.

The most important classes of oils and fats as sources of food are :—

I. *Animal Fats* and *Animal Oils*, excepting marine-animal oils, although whale oil is sometimes hydrogenated into a margarine fat (cf. Chapter IV, p. 57).

II. *Vegetable Oils*, especially the *non-drying oils*, typified by *olive oil*, and the *semi-drying oils*, typified by cotton-seed and maize oils, and to a less extent *drying oils*, typified by linseed oil.

III. *Vegetable Fats*, especially coconut oil, palm-kernel oil, various kinds of palm oil, cacao butter, etc.

I. ANIMAL FATS AND OILS

Tallow.—Ordinary "dripping" is simply an impure form of tallow, but the name "tallow" is generally used to denote the adipose fat or "suet" from sheep and oxen, being distinguished in commerce as mutton or beef tallow. The latter is somewhat softer in consistency, and is therefore more usually employed in the manufacture of margarine, though mutton tallow is also occasionally used. "Premier jus" consists of the less firm constituents of tallow, separated from the harder stearin by partial melting and pressure, as described in Chapter VII, pp. 93–95.

The chief sources of imported tallow are Australia, New Zealand, and North and South America. Some of the carefully picked tallow intended for margarine making is shipped to England "unrendered," but in some cases the fat is not only rendered, but also converted into "premier jus" abroad before shipment. Large quantities of tallow are also produced in Great Britain, and much of the rough fat is carefully hand-picked, rendered separately, and the product sold for margarine making.

The following figures (cf. p. 16) have been obtained for some typical samples of tallow :—

Tallows.	Saponification Value.	Free Acidity (as Oleic Acid) per cent.	Titre, °C.
Mutton :—			
Selected English . . .	197·6	1·45	47
Australian	197·4	0·48	48·3
South American . . .	197·3	1·11	47
North American . . .	197·5	1·32	44
Beef :—			
Selected English . . .	197·5	2·40	44
Australian	197·5	1·68	43·9
South American . . .	197·3	0·81	45
North American . . .	197·4	1·97	41·5

Lard.—This fat, obtained from the pig, is an important constituent of many butter substitutes, especially in the United States, whence most of that imported into this country is obtained. Its method of preparation and various qualities are fully described in Chapter VI.

Lard Oil, obtained by subjecting the softer varieties of lard to hydraulic pressure at a moderate temperature, is also dealt with in Chapter VI.

Some of the marine-animal oils, such as *whale oil*, have been used in Germany as constituents of margarine after hydrogenation into solid fats (see Chapter IV).

II. Vegetable Oils

Arachis Oil (Earth-nut or Pea-nut Oil).—This oil, used occasionally in margarine to reduce its firmness, and a useful table oil, is obtained from the nuts of *Arachis hypogœa*, a herb cultivated largely in North America, India, and Western Africa. Most of the oil is expressed in Southern France, and its chief use appears to be as an adulterant or substitute for olive oil, which it closely resembles in many respects. The principal test used for its detection is based upon the estimation of the proportion of arachidic acid (p. 142) in the fatty acids. The following values have been obtained with samples of the refined oil :—

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Acidity (as Oleic Acid) per cent.	Titre, °C.	Refractive Index at 20° C.
0·9175—0·9205	185·6—195	87—100·8	0·22—6·8	23·5—28	1·4712

Olive Oil.—Edible olive oil is obtained by expression from the fruit of the olive tree, and is largely used as salad oil, in cookery, and for tinning sardines. Olive trees are grown extensively in nearly all the countries bordering on the Mediterranean Sea, also to a considerable extent in California. The oil obtained from their fruit varies a good deal in quality, according to its source, oils from Leghorn or Gallipoli being the most esteemed. The following values have been recorded for genuine olive oils :—

Specific Gravity at 15 °C.	Saponification Value.	Iodine Value.	Acidity (as Oleic Acid) per cent.	Titre, °C.	Refractive Index at 15° C.
0·914—0·918	185—196	79—91·5	1·8	21	1·4704

Olive-kernel Oil closely resembles the pulp oil in its characteristics, and if expressed soon after the fruit has been gathered there seems no reason why the entire olives should not be expressed (see p. 104).

Other non-drying oils, which are similar in composition are *almond oil*, chiefly used in pharmacy, *apricot-kernel* and *peach-kernel oils* used as adulterants of almond oil, *hazel-nut oil* and *rice oil*.

Cotton-seed Oil.—This is obtained by expression from the seeds of the various kinds of cotton tree, grown extensively in America, Egypt, and India. A considerable quantity of the oil is expressed from the seed in this country, principally at Hull. The refined oil is used in making artificial butter, and also for culinary purposes. The best cotton-seed oil, used for margarine manufacture, is sold under the name of "butter oil."

The following values have been recorded for genuine samples of cotton-seed oil :—

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Titre, °C.	Refractive Index at 20° C.
0·9132—0·9250	191—195	109—116	32·2—37·6	1·4721

Maize Oil, expressed from maize, and obtained chiefly from the United States, where it is commonly termed "*corn oil*," is used as an edible oil, especially after hydrogenation. It is a golden yellow liquid with a characteristic odour of the grain, and, like cotton oil, is a typical semi-drying oil. It contains a considerable proportion of linolic acid, as is indicated by its iodine value.

Genuine samples of maize oil have given the following values :—

Specific Gravity at 15·5° C.	Saponification Value.	Iodine Value.	Acidity (as Oleic Acid) per cent.	Acetyl Value.	Titre, °C.	Refractive Index at 20° C.
0·9213—0·9268	188—193	113—128	0·40	7·8—12·5	17·2	1·4766

Sesamé Oil.—This oil is frequently employed in margarine manufacture, its use to the extent of 10 per cent. being compulsory in Germany and other countries, in order to simplify the detection of adulteration of butter with butter substitutes. It is largely expressed in Southern France from the seeds of the sesamé plant, which is grown in the Levant, India, Japan, and West Africa.

Representative samples have given the following results :—

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Acidity (as Oleic Acid) per cent.	Titre, °C.	Refractive Index at 20° C.
0·9210—0·9260	188—193	103—115	1·84	21·2—23·8	1·4568

Soya-bean Oil is expressed from the seeds of the soy plant (*Soja japonica*) which is cultivated in China, Japan, and India, and is now imported in large quantities into this and other European countries. It is not only used for edible purposes, but, as it has fair drying properties, is also used as a substitute for linseed oil in paints, etc.

It is composed of the glycerides of oleic and linolic acids with a smaller proportion of glycerides of solid fatty acids. The following values have been recorded for samples of undoubted purity :—

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Hehner Value.	Titre, °C.
0·9222—0·9279	190·6—192·9	118·2—135·4	95·5	23—25

Other semi-drying oils, which are used locally as edible oils, include *pumpkin-seed oil*, and *tomato-seed oil*.

Linseed Oil is primarily used as a drying medium for paints and varnishes, but is also used for food purposes in Poland, Russia, and other countries of the Near East. The flax-plant is also extensively cultivated in Egypt, the United States, and the Brazils.

It is characterised by containing a high proportion of the glycerides of linolenic and isolinolenic acids (see p. 14), together with those of linolic acid, oleic acid, and (in smaller quantity) solid fatty acids. Both the oil and the separated fatty acids yield insoluble bromides, and this is one of the most important tests of the purity of the oil.

The following values have been recorded for pure samples of linseed oil :—

Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Iodine Value.	Titre, °C.	Refractive Index.
0·9254—0·936	1·1	187·8—192·7	187—202·5	16·0—20·6	1·466

Sunflower-seed Oil is expressed from sunflower seeds, the principal source of which is Southern Russia and Caucasia. If care is taken in the cleaning and expression of the seeds, an oil which is fully equal to olive oils of the second grade is obtained. Of recent years the cultivation has been extended to South Africa.

Genuine specimens of sunflower oil have given the following analytical values :—

Specific Gravity at 15° C.	Acidity (as Oleic Acid) per cent.	Saponification Value.	Iodine Value.	Titre, °C.
0·924—0·926	0·81	188—193·3	122·5–136	18—19·8

Other drying oils which are used for food in Russia are *poppy oil* and *hemp oil*, obtained from the seeds of the respective plants, and *safflower oil*, which is extensively used in India both as a drying and culinary oil.

III. Vegetable Fats

Bassia Tallow, also known as *mohwah butter* or *mowrah-seed oil*, is expressed from the seeds of *Bassia longifolia;* whilst a similar fat, obtained from the seeds of *Bassia latifolia*, is known as *mahua butter* or *illipé butter*, the commercial product usually consisting of a mixture of the two fats.

Another Indian product, known as *phulwara butter*, is derived from the seeds of an allied species, *B. butyracea*, whilst the Dyaks of the Malay Peninsula separate an edible fat from the seeds of *B. mottleyana*.

Samples of these fats have given the following values :—

Fat from—	Specific Gravity at 99°/15° C.	Melting Point, °C.	Saponification Value.	Reichert Value.	Iodine Value.	Titre, °C.
B. longifolia .	0·8624	42	188·4—189·8	—	60·4—62·4	Commercial 38—40
B. latifolia . .	0·8595	28—31	192·2—199·9	0·44—0·88	59·4	—
B. butyracea .	0·8970 (100° C.)	—	188·2	0·44	42·1—47·7	—

The fat derived from the seeds of the Indian plant, *Buchanania latifolia* closely resembles mahua butter in its characteristics.

Borneo Tallow is derived from the seeds of several plants growing in Borneo, and notably *Shorea stenoptera*. Its odour is somewhat similar to that of cacao butter, for which it is sometimes used as a substitute under the name of *green butter.*

Cacao Butter is expressed from the beans of *Theobroma cacao*, which is grown in Central America, and is the source of ordinary cocoa. It is used in pharmacy, but is principally employed in the manufacture of chocolate cream (*vide* Chapter VIII, p. 114), the supply of which is very much inferior to the demand. At the ordinary temperature it is a yellowish white, brittle solid, bleaching with age. It has a characteristic odour of cocoa, and does not easily become rancid. It is composed largely of glycerides of saturated acids (about 60 per cent.), the mixed fatty acids containing about 40 per cent. of stearic acid.

The following analytical values were obtained with samples of various origin :—

Melting Point, °C.	Specific Gravity at 98°/15° C.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Titre, °C.	Refractive Index at 60° C.
26·6—33·6	0·8577	1·0—2·3	191·8—194·5	0·2—0·83	32·8—41·7	45—49·2	1·450

Coconut Oil is a valuable solid fat obtained from the nuts of the cocoa palm (*Cocos nucifera*), which grows in all tropical countries, and is especially cultivated in Ceylon, Cochin China, and the Philippines. The fat is either expressed on the spot, or the dried kernels (copra) are exported and the oil expressed in Europe or the United States. It is extensively used in the manufacture of margarine and of chocolate cream, and is also deodorised and sold under fancy names as a *vegetable butter.* There are two principal commercial varieties, "Cochin" and "Ceylon," the former obtained from

Cochin (Malabar) or the Philippine Islands, and the latter from Ceylon.

The poor quality of the oil expressed from certain grades of Philippine copra has been traced to the action of moulds prior to the expression. To prevent this, rapid drying is necessary.

Coconut oil consists principally of glycerides of volatile insoluble fatty acids, notably trilaurin and trimyristin, and of oleic acid, with smaller amounts of palmitin, caprin, and caprylin. It is therefore characterised by having a relatively high Reichert-Meissl value, and a high Polenske value, and these characteristics enable it to be identified in butter and other fats.

The following values are typical of those given by coconut oil :—

Melting Point, °C.	Specific Gravity at 99°/15° C.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Hehner Value.	Titre, °C.	Refractive Index at 25° C.
23—28	0·8736	253·4—262	6·65—7·5	6·2—9·95	82·35—90·5	21·2—25·2	1·4535—1·4540

Cotton-seed Stearine.—This is the solid residue remaining when the deposit obtained from ordinary refined cotton-seed oil by chilling is pressed. Its consistence is very similar to that of butter, and it is used in the preparation of some artificial butters. The oil left after separation of the stearine is known as " winter " cotton-seed oil.

Samples have given the following results :—

Melting Point, °C.	Specific Gravity at 99°/15° C.	Saponification Value.	Iodine Value.	Acidity (as Oleic Acid) per cent.	Titre, °C.
30—39	0·8684	194·8—195	88·7—93·6	0·95	34·9—35·1

Palm Oil.—This is obtained from the fruit of the palm trees grown extensively along the West Coast of Africa. There are many qualities, that from Lagos being the best. The oil is occasionally employed in the manufacture of margarine, to which it imparts a yellow colour. Some years ago its use was the subject of an action in the United States Supreme Court, the decision of which was that palm oil must be regarded as an artificial colouring matter, and must pay duty as such, even if used as a material ingredient to improve the wholesomeness and flavour of the product.

Commercial palm oil is usually a butter-like mass, varying in colour from orange-yellow to brown, and having a distinctive pleasant odour, which is lost when the fat is bleached with chemical agents.

The following values have been recorded :—

Specific Gravity at 99°/15·5° C.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Titre, °C.
0·8586	202—202·5	95·6	0·5	51—52·4	42·5—45·5

Palm-kernel oil has long been utilised as an edible fat, but for a long time all attempts to make use of any considerable quantity of the fat from the pulp of the fruit (palm oil) proved unsuccessful.

This was not on account of the deep orange colour of the fat, which could be readily removed by oxidation, but owing to the high proportion of free fatty acids.

The cause of this drawback was shown by Fickendey (*Der Tropenflanzer*, 1910, xiv. 566) to be due to the presence of an enzyme in the fresh fruit. For instance, the fat extracted from perfectly fresh fruit had an acid value of 94·5 to 116, which became still higher if the fruit was allowed to stand for twenty-four hours before the extraction of the fat.

By heating the fruit this enzyme is destroyed, and the fat will then show a low acid value. Thus in four instances in which this was done the acid value did not exceed 5·3.

Fickendey concluded from these experiments that it would be quite possible to put a palm oil of good quality upon the market, provided that the following conditions were observed :—(1) Expression of fresh, completely ripe fruit; (2) destruction of the enzyme by boiling; (3) rapid treatment of the fruit. The last condition is essential, owing to the readiness with which micro-organisms will decompose the fat in the heated fruit.

Palm-nut Oil (Palm-kernel Oil).—This fat is obtained by expression or extraction in Europe from the kernels of the palm-tree fruit imported from Africa. It very closely resembles coconut oil in character and is used for similar purposes. The following results have been obtained with normal samples of palm-kernel oil :—

Specific Gravity at 99°/15° C.	Melting Point, °C.	Saponification Value.	Iodine Value.	Titre, °C.	Refractive Index at 25° C.	Hehner Value.	Reichert Value.
0·8731	23—28	243—247	10·3—17·5	20·0—25·5	1·4553	91·1	2·5

Numerous species of palm trees produce fats, which have as yet hardly become commercial products. For example, in the forests of Brazil there are immense supplies of fat from this source, which are only just beginning to be utilised. The fats derived from the ordinary palm tree (*Elæis guineensis*) of Brazil differ materially from those produced by the corresponding African tree. The fruits of other trees (pulp or kernel) yield fats which could well be utilised in the manufacture of margarine or as substitutes for cacao butter. These include the products of various trees of the *Astrocaryum* species, the *Anajá* or *kokerite palm*, and *Acrocomia sclerocarpa*, growing in the forests of Paraguay, and the fruit of which contains a fat similar to palm oil.

The close resemblances between the chemical and physical characteristics of new fats such as these, increase the difficulties of fat analysis, since they render it practically impossible to do more than determine to which class of fats a given sample belongs.

Shea Butter.—This is extracted from the kernels of *Butyrospermum* (or *Bassia Parkii*), grown in Africa and Eastern India. It is used by the natives as a food, and is exported to Europe, where it finds a use in the manufacture of lard substitutes and chocolate fats. It is somewhat tough and sticky, and has the following properties, the proportion of unsaponifiable matter being exceptional.

Melting Point, °C.	Saponification Value.	Acidity (as Oleic Acid) per cent.	Titre, °C.	Refractive Index at 60° C.	Iodine Value.
41·2	186·9	8·2	53·2	1·4566	58·9

CHAPTER III

EXTRACTING, REFINING, BLEACHING, AND DEODORISING FATS AND OILS

Separation of Oil—Expression—Hydraulic Presses—Kettles—Rolls—Extraction of Oil—Refining—Bleaching and Deodorising—Physical Methods: Washing, freezing, filtration, treatment with charcoal and fuller's earth, steaming. Chemical Methods: Caustic soda, sodium carbonate and silicate, alkaline earths, ozone, hydrosulphites, sodium bisulphite, hydrogen, organic peroxides.

Expression of Oil.—The methods of separating the oil from the vegetable or animal tissues in which it is contained may be classified into *rendering by heat*, *expression* with or without the aid of heat, and *extraction* with solvents. In the first method the material is heated to a suitable temperature, sufficient to rupture the cell membranes without decomposing the fat to any notable extent, and the oil which then exudes from the cells is drained off and clarified. This method is typified by the preparation of lard (see Chapter VI).

An analogous process of great antiquity is still used in many tropical countries for the separation of oil from fruit-pulp and nuts, the material being first pounded or crushed and then boiled with water, so that the oil rises to the surface and can be skimmed off. In some places nuts are first roasted before being crushed and boiled with water, this process facilitating the subsequent separation of the oil.

Primitive forms of presses for separating the oil from fruit-pulps, such as olives and palm fruit, are still employed in many parts of the world, the residual mass being then boiled with water and again expressed. Analogous processes are also in use for extracting oil from fish and the livers of fish such as sharks.

Hydraulic Presses.—The older forms of screw presses which are worked by means of belts communicating with a horizontal shafting from a steam engine, have now, to a large extent, been superseded by hydraulic presses. In the ordinary type of hydraulic press, water is admitted into the cylinder either intermittently by means of pumps, or continuously from an accumulator. For some purposes horizontal presses are sometimes preferred.

In the "Anglo-American System" the press is vertical, and contains a series of corrugated plates arranged at a sufficient distance from each other to permit of the introduction of the moulded cakes of hot ground seed, etc., coming from the kettle and moulding machine. These plates are either supported by means of links or by racks.

"*Cage*" *or* "*Clodding*" *Press.*—This name is given to a form of press which is in common use for the preliminary expression of oil from such material as castor seeds, copra, or palm-kernels. The crushed meal coming from the kettle is delivered into a cage or cylinder constructed either of staves with interstices, through which the oil exudes, or of perforated steel. In the "Leeds" system the cages are formed of vertical bars held together by steel hoops, and the spaces between these bars can be regulated to suit the material.

If much oil is present, as in the case of copra and castor seeds, clodding presses are often used for the first expression, whilst a press of the Anglo-American type is used for the second and third expressions. The quality of the oil will vary with the mode of expression. In the case of olives, for example, the finest product is the "cold-drawn" oil, which is obtained by expression in the cold. The oil-cakes in the press are then again ground, slightly moistened with water, and pressed again, whereby a second quality of cold-drawn oil is obtained. The residual oil-cakes are next ground up and heated and expressed while hot to obtain a third grade of oil, whilst the final residue is subjected to a process of extraction with a solvent to recover the oil which it still contains.

Crushing Rolls and Edge-runners.—Prior to the expression the seed is delivered into the hopper of a series of crushing rolls, usually five in number, which are brought into contact by a combination of springs, so that a regulated uniform pressure can be obtained. For the crushing of certain materials, such as copra and cotton seed, heavy edge-runners of stone are often used in place of rollers.

Kettle.—The "kettle" used in the Anglo-American system is a circular cast-iron vessel, heated by means of a steam jacket, and provided with an internal agitator, to keep the material in motion during the heating. The crushed seed from the rolls is delivered into the kettle by means of an elevator, or in some cases the crushing apparatus is fixed above the kettle. After being heated, the material is compressed into thin blocks or cakes in a moulding machine, and these are expressed in presses of the types described above.

Extraction of Oil with Solvents.—In recovering the oil from the final residues from the press the solvents most frequently used are petroleum spirit, carbon bisulphide and the chlorine derivatives of hydrocarbons, such as carbon tetrachloride, chloro-ethanes, or ethylene chlorides. The solvents of the last-mentioned class have the advantage of being non-inflammable, but since there is always some unavoidable loss in the recovery of the solvent are more expensive to use.

Carbon bisulphide is still extensively employed for the extraction of the final residue (*marc*) from the expression of olives, but the extracted oil, technically termed *sulphur* or *bisulphide oil*, acquires an unpleasant taste from the solvent. Hence, petroleum spirit, although more expensive, is more frequently used for the extraction of oils in general.

The vessels used for the extraction are either used simply or in batteries of several extractors. For continuous extraction in a single vessel the extractor is provided with a false bottom on which the material rests, and is heated by a steam coil or other device. This vessel is connected with an evaporator, into which the solution of oil is drawn off, and evaporated, the oil being left as a residue, whilst the vapours of the solvent are condensed in an attached cooling coil, and returned to a storage tank, whence they flow back again into the extractor. This process is continued in a cycle until the whole of the oil has been removed from the material.

In the other method of extraction the solvent is made to flow through the series of extractors, each of which has been charged with the material. When the contents of one vessel have been extracted, that member of the series is withdrawn from the circuit and recharged, without interrupting the process in the others. The solvent leaving the last vessel in the series is rich in oil, which is separated by evaporating the liquid in a vesesl heated by means of a steam coil, and connected with a condenser, for the recovery of the solvent.

Purification of Oils.—Although, as was pointed out in Chapter II, too much stress cannot be laid upon the importance of using only the freshest materials of the best possible quality in the manufacture of edible fats, yet even these frequently require a certain amount of preliminary treatment in order to bleach, deodorise, or refine them and render them palatable for human food. Numerous processes, both physical and chemical, have been devised, and in many cases patented, for these different purposes, and the following is a summary of the more important ones.

Physical Methods.—Among the physical methods employed may be mentioned washing with hot water, the removal of suspended matter by settling or filtration, and of excess of stearin by subjection to low temperatures, bleaching by filtration through animal charcoal or fuller's earth, and deodorising by injecting steam either at atmospheric pressure, *in vacuo*, or in presence of an indifferent gas.

The impurities in freshly expressed oil, which are partly in suspension and partly in solution, consist chiefly of dirt, fragments of vegetable fibre, and mucilaginous and albuminous substances. A portion of them rapidly deposits when the oil is allowed to stand, and the upper liquid may then be drawn off from the sediment, and subjected to filtration or to further refining processes.

In some cases a simple filtration, after standing for a short time, is sufficient to render the oil brilliant, but special treatment is necessary when a large proportion of albuminous matter is present, since such oils either pass through the filter without becoming bright, or if a closer filtering medium is used, the pores of the filter speedily become clogged.

Various methods are employed to coagulate or precipitate albuminous matters before filtration, such as dry heat, or the introduction of fine jets of steam, or the addition of a small quantity of insoluble powder (*e. g.* fuller's earth or *kieselguhr*), which as it subsides attracts and carries down simultaneously the particles of the gum-like mucilage.

The formation of an insoluble precipitate within the oil answers the same purpose. Thus, in Linde's process a small quantity of milk is introduced and the mixture heated so as to coagulate the casein, the subsidence of which removes at the same time the substances which cause turbidity in the oil.

Other substances, such as solutions of tannin, are used in the same way in refining oils for technical purposes, but are inadmissible in the cases of edible oils.

In the removal of dissolved impurities, alkali solutions, milk of lime, or magnesia are reagents in common use, while dilute sulphuric acid is employed to clarify linseed and certain fish oils for industrial uses.

To facilitate the purification of oils by washing with water, Dubovitz has recommended the addition to the water of aluminium sulphate, in the proportion of about ¾-oz. to 220 gallons per degree of hardness. This forms with the lime in the water a bulky, colloidal precipitate, which serves to bleach and clarify the oil.

Removal of Stearine.—When certain oils are exposed to a low temperature they become turbid and in some cases give a white deposit. This consists of glycerides of the more solid fatty acids, and is known as "stearine," and its formation is frequently regarded as objectionable, notwithstanding the fact that when the oil is gently heated the stearine is redissolved.

In the preparation of the best edible oils, therefore, a process of chilling followed by filtration is often employed in order to remove part of the stearine, and the oils thus treated may then be exposed to a low temperature without giving a further deposit.

Oils treated in this way are commonly known as "winter oils," and those which will only keep brilliant at the ordinary summer temperature are termed "summer oils."

The solid fat separated in this way from cotton-seed oil is known as cotton-oil "stearine," although it is quite free from stearic acid. A similar process is employed for the separation of coconut and palm-kernel oils into their respective stearine and oleines (see *Chocolate Fats*).

Methods of Filtration.—The types of filter press used in the filtration of oils are very varied. A common form consists of an hydraulic press containing a series of communicating plates with rims raised so as to form a space into which filter cloths may be fitted.

In other forms of apparatus the oil is introduced from below into a chamber, and rises upwards through the filtering medium into a compartment in which a partial vacuum has been created. Or methods of centrifugal filtration may be employed, as in apparatus in which the oil is introduced into a revolving chamber with a perforated wall round which is wrapped a filtering cloth. The oil is flung against the wall of the revolving chamber in a fine state of division, and passes through the filtering medium into an outer chamber, whence it can be drawn off.

The materials used as filtering media include sand, *kieselguhr*, Spanish clay, fuller's earth, animal charcoal, paper pulp, and a mixture of wool and vegetable fibres disintegrated into a pulp.

Chemical Methods.—The number of chemicals employed in refining oils and fats for edible purposes is necessarily very limited. It is of course very objectionable to employ any reagent which is poisonous, whilst the use of barium oxide has been patented by Rocca (Fr. Pat. 325,381, 1902), and processes involving the use of mineral acids are, in general, inadmissible, as they spoil the flavour of the oil. The chief reagents employed are caustic soda (sodium hydroxide), sodium carbonate, sodium silicate, calcium or magnesium oxide, ozone, hydrosulphites, formaldehyde-sulphoxylates, and organic peroxides.

Caustic Soda.—Of the alkaline refining process the treatment of cotton-seed oil with a solution of sodium hydroxide or potassium hydroxide is the best example. The oil is mechanically agitated with the alkali solution, which usually has a specific gravity of about 1·10, either with or without the aid of heat, and the mixture then allowed to stand until it separates into two layers, the lower of which contains a sediment of impurities. This is drawn off, and the treatment repeated, but this time with a more dilute solution of alkali, and finally the oil thus clarified is washed with water to remove the excess of alkali.

In this process of refining not only are the albuminous and resinous matters precipitated, but the free fatty acids in the oil are neutralised, and accordingly freshly prepared cotton-seed oil is almost neutral in its reaction, and has a bland taste. The treatment also removes a large proportion of the colouring matter separated from the seed in the expression of the oil, and changes the dark-brown colour of the crude product to a light golden tint.

The residue left from the refining of cotton-seed and other oils is a thick deposit containing the impurities in a concentrated form, together with a considerable proportion of oil; such residues are known as "foots," and are utilised in the manufacture of soap.

The amount of caustic soda required depends on the degree of acidity of the oil, which it should be just sufficient to neutralise. The acidity of the oil is therefore first determined, as described in Chapter IX, and the quantity of caustic soda calculated which will neutralise the given bulk of oil to be treated. The following is a more detailed account of the process :—

The calculated quantity of alkali is dissolved in water, the solution diluted to 12° or 15° Tw. (8° or 10° B.), and one-third of it added, either in a fine stream, or through a sprinkler, to the oil contained in a steam-jacketed tank. The mixture is now heated first to 100° F., and then gradually to 120° F., the whole being well agitated mechanically, or by blowing a current of air through a pipe inserted to the bottom of the tank.

After about fifteen minutes the agitation is stopped, and the oil allowed to rest for some time, preferably overnight, to allow the soap and impurities to settle down to the bottom, whence they may be drawn off. This treatment is then repeated a second and third time, with the same quantity of caustic soda solution, but usually of weaker strength, and in exactly the same manner as just described, after which a clear, yellow oil should be obtained.

The agitation with air must not be unduly prolonged, as this tends to oxidise the oil, raising its specific gravity and refractive index, lowering its iodine value, and also injuring its flavour.

Treatment with caustic soda solution is also frequently employed for refining other vegetable oils, notably coconut oil. In all cases the principle is the same, viz., combination of the alkali with the free fatty acids to form soap, which on settling carries down with it colouring matter and other impurities. Only a weak solution, of say 12° Tw. (8° B.), should be used, and the quantity added should not be more than sufficient to neutralise the free acid, since otherwise some of the neutral oil may be saponified.

Emulsions are sometimes formed in this treatment, but are easily broken up by the addition of brine.

Sodium Carbonate.—This may be employed instead of caustic soda to neutralise the free fatty acids of an oil or fat. In practice, however, it is less frequently used by itself for refining purposes, though there is less risk of saponification of the neutral oil if a slight excess is added than in the case of caustic soda.

A process has been patented in France by G. Müller (Fr. Pat. 334,336, 1903) for the treatment of cacao butter with sodium bicarbonate. The fat is heated with sodium bicarbonate and water, then cooled with constant agitation until it congeals, allowed to stand for twenty-four hours, and finally subjected to a process of pressing and kneading. The fat thus treated is claimed to be softer and less brittle.

Sodium Silicate.—This is an alkaline salt, and its action is very similar to that of sodium carbonate. Its use for bleaching oils and fats has been patented by Godard (Eng. Pat. 22,085, 1903), who mixes the oil with sodium silicate, separates the soap formed, and then deodorises the neutral oil by means of steam in a fine state of division.

Alkaline Earths.—Lime and magnesia are sometimes used for removing the free fatty acids from oils and fats, insoluble calcium and magnesium soaps being formed. In Rocca's patent, to which reference has already been made (vide *supra*), the oil is first neutralised with caustic soda or sodium carbonate, decanted from the resulting soap, a small quantity of strong acid added to decompose any soap remaining, and the oil finally neutralised with lime, magnesia, or baryta.

Fresenius (Eng. Pat. 19,171, 1902) neutralises the oil with caustic soda, lime, or magnesia, under a pressure of two or three atmospheres, either in the presence of carbon to prevent oxidation, or according to a later process in an atmosphere of an inert gas. It is claimed that the increased pressure facilitates the separation of the soap emulsion.

Bleaching of Oils.—The colouring matter of crude oils consists of chlorophyll, which gives them a greenish tinge; or of substances frequently of a resinous nature, which impart a brown colour.

In the case of some oils, such as olive oil, the natural greenish tint is allowed to remain, but the dark colour of certain other crude oils has to be reduced before the product is saleable.

As was mentioned above, treatment with alkali removes from cotton-seed oil a large proportion of the dark colouring matter at the same time as the constituents that cause turbidity.

The methods in which fuller's earth or milk is used to refine oils have also some effect in producing a filtrate of lighter colour, whilst a treatment with freshly prepared animal charcoal is effective as a decolorising process in some cases.

Charcoal.—Bleaching with charcoal may be effected by mixing the oil with 1 to 5 per cent. of *animal* charcoal, in a granular form, warming for a short time, and filtering through a filter press. The bleaching action of animal charcoal, attributed by Knecht to the presence of nitrogen compounds, is greater in the presence of acid.

Crude charcoal requires preliminary treatment before being used for bleaching purposes. It should be well boiled, first with pure water, and then after the addition of sufficient sodium carbonate or hydroxide to render it alkaline. It is next washed free from alkali, and boiled for twelve hours with four times its weight of a mixture of equal parts of commercial hydrochloric acid and water, after which it is washed free from acid, dried, and burned in closed vessels. A good bleaching charcoal is thus obtained.

Fuller's Earth.—Fuller's earth (aluminium magnesium hydrosilicate) should be dehydrated by roasting prior to use, in order to secure the best results. The quantity required varies from 2 to 5 per cent. for coconut, palm-kernel, and olive oils, to upwards of 10 per cent. for arachis and cotton-seed oils, and the oil should be thoroughly mixed with the reagent and maintained at a temperature of say 100° F. for about fifteen minutes, and then filtered through a filter press. The fuller's earth retains about 80 per cent. of the oil, which may be extracted by means of a solvent, the latter distilled off, and the recovered oil treated with a fresh quantity of fuller's earth. The spent fuller's earth may be "regenerated" by heating it up to 400° to 500°. Fuller's earth is frequently used in America for the filtration of "premier jus."

According to Hirzel (*Chem. Rev. Fett Ind.*, 1904, 116–118; 145–146), the earthy flavour sometimes remaining after contact with fuller's earth may be removed by washing with 10 per cent. of a 10 per cent. solution of brine, and by adding 1 to 1½ per cent. of powdered, dry sodium bicarbonate.

Godard (Eng. Pat. 22,086, 1903) carries out the agitation with reagents *in vacuo* in order to prevent oxidation of the oil.

No very definite details as to the quantity of charcoal or fuller's earth to be used, the temperature to which the oil should be raised in contact with them, and the time it should be maintained thereat, can be given, as these vary considerably for different oils, and can only be determined by actual experiments with the particular oil it is required to bleach.

The use of finely divided alumina, bauxite, or magnesite previously ignited at a low temperature, has also been patented for decolorising oils, and a process for the recovery of spent decolorising materials (which consists in mixing them with salt water, heating the mixture to about 85° C. with sulphuric acid, then treating it with sodium carbonate and mechanically agitating it for a short time) has been patented by the Soc. Anon. Huilerie et Savonnerie de Lurian (Fr. Pat. 499,915, 1909). The carbon dioxide liberated by this treatment carries the oil to the surface.

Methods in which chlorine or bleaching powder are employed are only applicable for bleaching oils intended for the making of soap or other technical purposes, owing to the reagent attacking the glycerides and imparting a flavour. For similar reasons Watts's bichromate process of bleaching palm oil is also unsuitable for the treatment of fat intended for food.

Methods of oxidation, either by means of hot air passed through the heated oil or fat, or by means of ozone or ozonised air, under controlled conditions, are employed both to obtain paler oils and to remove substances of unpleasant odour.

The bleaching of beeswax by exposing it in thin strips to the action of air and sunlight has long been practised, and Japan wax is also rendered nearly white by similar means.

The use of artificial light in place of sunlight is claimed in several patents for bleaching oils, such as cotton-seed oil. The oil is made to pass across a transparent surface through which are transmitted the rays from a powerful arc light.

Ultra-violet rays, such as those emitted by the mercury vapour lamp, are employed as the bleaching agent in similar processes.

Ozone.—The use of ozone as a bleaching agent has long been known, but its application to the treatment of oils and fats met with little success for many years. It has been the subject of many patents, among which may be mentioned that of Andreoli (Eng. Pat. 14,570, 1898), who makes use of the joint action of ozone and a hypochlorite solution, and that of J. Harris (Eng. Pat. 22,430, 1906). Harris first ozonises the oil at a temperature of 100° to 180° F. for fifteen to thirty minutes, until there is an appreciable rise—say 0·5 per cent.—in the amount of free fatty acids. The treatment with ozone is then stopped, and the oil neutralised with alkali, preferably an aqueous solution of caustic soda at about 15° Tw. (10° B.). The impurities are next separated, and the oil dried by means of a current of air while warm, after which it may be still further refined by heating it with 5 per cent. of aluminous earth, followed by filtration.

This latter process seems to be rather a mistaken one, as from experiments made by one of the authors (S.), the best results are obtained when the ozonisation is only carried to such a point that there is no appreciable increase in the free acidity of the oil.

Experiments by him on the bleaching and deodorising action of pure ozone *free from nitrogenous compounds*, as obtained with the Ozonair apparatus, have given results which are most promising. Palm oil, even of the crudest description, has been most effectively and cheaply bleached by merely passing a strong current of ozonised air through it, and the colour of certain other vegetable oils has been distinctly improved by this treatment; whilst in the case of a very acid sample of coconut oil, the fat was not only made whiter in colour, but had also almost entirely lost its characteristic odour. Hence there seems to be a likelihood of the successful employment of the ozone process for this purpose in the future.

Hydrosulphites, or " Hyposulphites."—Sodium hydrosulphite, obtained by digesting a concentrated solution of sodium bisulphite with zinc dust or turnings, is a powerful reducing agent, and has been patented as a means of bleaching oils and fats by Metz and Clarkson (Eng. Pat. 11,983, 1906). It is particularly applicable to maize oil, which may be bleached by agitating 200 parts of the oil with 600 parts of water and 15 parts of sodium hydrosulphite for ten hours in a closed vessel, allowing the mixture to stand for thirty-two hours, and then separating the oily layer.

Sodium hydrosulphite formaldehyde, which was shown by Baumann, Thesmar, and Frossard in 1904 to be commercially a mixture in almost equal proportions of sodium sulphoxylate formaldehyde and sodium bisulphite formaldehyde, is also recommended for the purpose, the oil being heated to 70° C. with this reagent in a closed vessel, and then allowed to stand.

The formaldehyde-sulphoxylates are now sold under a variety of fancy names, the sodium compound being termed *Rongalite C.* and *Hydraldite C.*, and the zinc salt *Decroline.*

Sodium Bisulphite.—This salt, which possesses the property of combining with aldehydes, had been utilised in some cases for deodorising oils and fats, with good results.

Organic Peroxides.—The Vereingte Chem. Werke have patented the use of various organic peroxides (such as those of benzoyl, acetyl, and acetone, together with the oxidation products obtained by the action of nitrogen tetroxide on organic compounds) for the bleaching of oils and fats. The oil is heated to 100° C. with about 0·2 per cent. of the peroxide, and allowed to stand in a warm place for a short time, until bleaching has taken place.

There is now a large number of per-salts available, *e. g.*, persulphates, percarbonates, perborates, which are being utilised for various bleaching purposes, but so far they do not appear to have been employed to any considerable extent in the treatment of oils and fats, though ammonium persulphate (palidol) is now being used for bleaching soap in the pan.

Deodorisation of Fats.—The odours of oils and fats are due to the presence of small quantities of volatile substances, either derived from the vegetable substance as in the case of maize and wheat oils, or formed by slight decomposition of the oil itself.

It is chiefly in connection with coconut oil, which forms the basis of so many vegetable lards and butters, that the problem of deodorisation of a fresh fat has to be faced.

According to the research of Haller and Lassieur (*Comptes Rend.*, 1910, 150, 1013), the unpleasant odour of commercial coconut oil must be attributed, partly to a process of decomposition of the glycerides, with the liberation of fatty acids (caproic, caprylic, capric acids, etc.) with a pronounced odour; and partly to the presence of certain substances, which include methylheptylketone and methylnonylketone. Traces of these may also be detected in the refined fat, and account for its odour when heated. The substances to which the odour is due may be obtained in the form of an essence (*échappés*) by distilling the coconut oil in a current of superheated steam.

Speaking broadly, two methods only have so far been discovered, or, at any rate, published, for the deodorisation of coconut oil—(1) washing out of the odoriferous bodies with alcohol, and (2) their volatilisation by treatment with steam. Other unpublished processes are doubtless used by some manufacturers, but their secrecy is very jealously guarded.

The washing of coconut oil with alcohol obviously removes free fatty acids, which are soluble therein. This method of treatment was first introduced by Chevreul, and has been also utilised by Schlinck, who employed a joint process of washing with alcohol and treatment with charcoal. A special apparatus for its application was patented by Urbain and Feige (Fr. Pat. 361,966, 1905), consisting of a series of vessels so arranged that the oil descends from vessel to vessel, and meets hot alcohol circulating in the opposite direction, so that the more impure oil comes in contact with the more impure alcohol. The temperature is maintained at 70° C. during the treatment, and means are provided for evaporating and condensing the alcohol after extraction is complete.

An improvement upon this patent has been since protected by the patentees, in which sufficient alkali is added to combine with the free fatty acids prior to the extraction with alcohol.

With so volatile a substance as alcohol, there is necessarily a considerable loss by evaporation during working, and the cost of alcohol in this country is too high for the process to be economical.

The treatment of coconut oil with steam in order to deodorise it dates back to 1882, when a process was patented in Germany by Jeserich and Meinert, in which the volatile fatty acids were first driven off by passing high-pressure steam at six to eight atmospheres into the fluid oil, with constant stirring for about two or three hours, after which steam was shut off, and the non-volatile fatty acids separated by addition of 0·25 per cent. of calcined magnesia, the magnesium soap formed rising to the surface, whence it could be skimmed off.

Several modifications of this process have since been patented. Klimont (Eng. Pat. 3164, 1902) neutralises the oil with alkali prior to treatment with superheated steam, and then removes non-volatile impurities by either raising the temperature of the oil to above 100° C., treating it with calcium or magnesium hydroxide, or extracting it with some solvent such as acetone, which dissolves the oil and precipitates the impurities.

The Fabrique de Prod. Chim. de Thann et de Mulhouse treats the oil with steam in the absence of air, either *in vacuo*, or in an atmosphere of an indifferent gas.

In another method of deodorisation coconut oil is freed from its more fluid constituents (as in the preparation of chocolate fats, *q.v.*) and the fatty acids eliminated in the form of calcium salts by treatment with lime; sodium silicate is employed in another process as the means of removing the fatty acids. Yet however carefully the odoriferous substances may have been removed, the readiness with which coconut oil undergoes hydrolysis, and the nature of the fatty acids contained in its glycerides, renders this fat particularly liable to acquire an odour again, after having been exposed for a short time to the air.

Catalytic hydrogenation effects not only the solidification of an oil, but also its deodorisation and methods in which hydrogen is used without a catalytic agent have also been stated to have a similar deodorising action.

Treatment of Rancid Fats.—Although the practice is to be condemned, it is not uncommon for fats which have become slightly rancid to be subjected to treatment to eliminate the compounds to which rancidity is due, and thus enable the fat to be blended with fresh fats.

Fatty acids were first driven off by passing high pressure steam at six to eight atmospheres into the fluid oil, with constant stirring for about two or three hours, after which steam was shut off, and the non-volatile fatty acids separated by addition of 0·25 per cent. of calcined magnesia, the magnesium soap formed rising to the surface, whence it could be skimmed off.

As in the treatment of coconut oil (p. 49), there are several modifications of the process, such as treatment of the oil with alkali prior to treatment with superheated steam, to make the oil appear fresh. This may be effected by mechanically agitating the fat with a suitable proportion of milk of lime or magnesia, which combine with the free fatty acids to form insoluble calcium or magnesium soaps, readily separated by filtration.

Neutralisation with caustic alkali (as in the refining of cotton-seed oil) or with a solution of sodium silicate, also effects the removal of free fatty acids, but the latter reagent is liable to produce an obstinate emulsion when employed on a large scale.

In another process the rancid oil is treated with a suitable proportion of precipitated chalk, and is subsequently filtered while hot through a layer of animal charcoal.

Reference has already been made to the method of dissolving out the free fatty acids by means of alcohol. Oils in which a process of hydrolysis has once started are liable, after removal of the free fatty acids, not to keep so well as freshly expressed products.

Rancidity may be present in an oil without the liberation of free fatty acids, though, as a rule, the acid value of a fat will afford some index of the degree of rancidity, since the development of acidity and of rancidity are often simultaneous.

For the removal of the aldehydic compounds formed in the changes that occur, a treatment with a strong solution of sodium bisulphite is used in a process described by Nagel, while volatile products are expelled by heating the oil in a current of steam at gradually increasing temperatures.

Other reagents used for sweetening rancid oils are a solution of ordinary salt, dilute (1 per cent.) sulphuric acid, a solution of myrrh in methyl-alcohol, etc.

As a rule, the different processes are employed successively, and followed by filtration and drying of the oil.

The tendency of an oil to become rancid depends largely upon the proportion of volatile fatty acids and unsaturated fatty acids it contains. Thus butter and coconut oil readily turn rancid, whereas beef stearin and cacao butter will keep for a long time unaltered.

Any oil or fat is best protected from rancidity by keeping it in the dark in a vessel from which all air is excluded. Rancidity will take place in the dark, but much less rapidly than when the fat is exposed to light. This is due to the accelerating effect of light upon the action of oxygen. Heat has also a pronounced influence in promoting chemical changes in oils, and cold has a retarding influence, although it does not stop the oxidation.

The odour of rancid fats which do not (like coconut oil) contain volatile fatty acids is due to the formation of aldehydes or of esters, the latter being probably produced, in some cases at all events, by the action of certain micro-organisms upon the liberated glycerin.

Rancidity is accompanied by a decrease in the iodine value of the fat, which is due to the absorption of oxygen by the unsaturated bonds of the liquid fatty acids. A determination of this value may therefore, in some cases, give indications of the freshness of a fat.

A better method, however, is to distil the fat in a current of steam, and to estimate the amount of aldehydes in the distillate. In a method recently devised by Issoglio the volatile compounds are distilled in a current of steam, and the distillate is titrated with standard permanganate solution, the amount of which used under specified conditions is termed the *oxidisability value* of the fat, and rises with the increase of rancidity in the fat.

A biochemical test for rancidity has been based upon the fact that fats absorb oxygen in becoming rancid, and will then give a blue coloration with guaiacum tincture and an aqueous solution of blood or hæmoglobin.

CHAPTER IV

HARDENED OR HYDROGENATED OILS

Catalytic Hydrogenation.—The solution of the problem of converting fluid oils into solid fats may be regarded as the greatest advance which has taken place in the industry during the last few years.

Although repeated attempts had been made to obtain a solid material from liquid fatty acids, such as by fusing oleic acid with potassium hydroxide, or by treating mixed fatty acids with sulphuric acid or with zinc chloride, the results were only partly successful, and the products were only suitable for technical purposes such as manufacture of candles.

It was not until Sabatier and Senderens showed, in 1900, that the presence of an inert substance, such as palladium, caused hydrogen to be absorbed by unsaturated compounds, that the solution of this difficulty was found.

In 1903 Normann patented a process of hydrogenating oils and fatty acids by bringing them into contact with hydrogen in the presence of finely powdered nickel or other catalytic agent, at a suitable temperature. Since then there has been a steady succession of patents for carrying out this process of hydrogenation, and the conditions for the reaction have been thoroughly investigated.

The use of metallic palladium as the catalyst was patented in 1911 (Eng. Pat. 18,642) and is claimed to be much more effective than nickel.

The catalytic agent appears merely to act as the medium for bringing the hydrogen into such contact with the finely divided oil, that it is able to combine with it, which without such intervening agent it will not do, and the catalyst itself apparently remains practically unaltered during the reaction.

In the case of oleic acid, for example, the absorption of hydrogen may be represented as follows—

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + H_2 = \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}$$

Similarly in the case of glycerides, olein is converted into stearin, and the other glycerides of unsaturated acids into those of the corresponding saturated fatty acids, the degree of hardening depending upon the duration of the hydrogenation.

Hydrogenating Apparatus.—The forms of apparatus in which the intimate of association of the finely divided oil, hydrogen, and catalyst is brought about, are very numerous, and fresh modifications are continually being patented.

In Kayser's apparatus (U.S. Pat. 1,004,035, 1911) the hydrogenation is effected in a closed cylinder in which revolves a paddle wheel, the blades of which are covered with wire gauze, while means are provided for heating the contents of the vessel to about 150° to 160° C.

In order to carry out the process at a somewhat lower temperature, Wilbuschewitz (1912) devised an apparatus consisting of a series of connected autoclaves, into which the oil and catalyst was admitted as a fine spray and encountered a current of hydrogen at about 100° to 160° C.

Other forms of apparatus are those of Schlink and Co.

(Eng. Pat. 8147, 1911) consisting of a series of drums containing porous catalytic material, and of Ellis (U.S. Pat. 1,026,156, 1912) in which the porous catalyst is placed in tubes which can be heated at any point.

Hydrogenation is effected under pressure in Testrup's apparatus, whilst in Borkeland and Devik's process (U.S. Pat. 1,125,259, 1915) a mixture of the oil and catalyst is forced from a jet into an atmosphere of hydrogen and so downwards into the main body of the oil, whereby the hydrogen is liberated and absorbed as it rises again.

Lane's apparatus (Eng. Pat. 968, 1915), which is widely used in this country, consists essentially of a vertical cylinder heated by means of a steam jacket or other device. The oil is introduced at the top, and is alternately sprayed outwards to the sides by means of beaters revolving round a central shaft, and thrown back again to the centre by means of annular sloping shelves between each series of beaters, and so on, until it reaches the bottom and is pumped up to the top again.

The Catalytic Agent.—Nickel or an oxide of nickel is the agent most frequently used as the catalyst, for palladium and platinum are, as a rule, too expensive for industrial processes. Numerous methods of preparing the catalyst have been patented, the object being to obtain it in as fine a state of division as possible, upon a porous medium, and in pure condition. The presence of powdered metals (not reduced by hydrogen), such as nickel, tin, zirconium and copper, have no injurious action, but iron, zinc, lead and mercury have a "toxic" effect upon the hydrogenating process.

It is also essential that the hydrogen should be very pure, and in particular that it should be practically free from chlorine, sulphur, phosphorus and arsenic, and contain not more than traces of oxygen and carbon oxides.

Preparation of the Hydrogen.—In Lane's process the hydrogen is obtained by conducting steam over red-hot iron—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2,$$

and the iron oxide is then again reduced by means of a gas, such as producer gas containing carbon monoxide—

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2.$$

The two processes may be carried out successively, provided that a sufficient velocity of reaction is maintained. (Eng. Pats. 10,536, 1903; 17,591, 1909; 11,878, 1910.)

Another method of preparing hydrogen is that of Linde, Frank, and Caro, in which water-gas is liquefied and distilled, and the hydrogen fraction purified by being passed over soda-lime previously heated to 180° C.

A very pure hydrogen, containing only about 0·2 per cent. of oxygen as impurity, is obtained by the electrolytic decomposition of water rendered faintly acid (with sulphuric acid) or alkaline.

In a process used by the Griesheim Elektron Company, water-gas is decomposed by means of a mixture of lime and iron, whilst in countries where a supply of petroleum is available, the Rincker-Wolter process, in which the hydrocarbons of oil-gas are decomposed at a high temperature into carbon and hydrogen, is available.

Hardened Fats.—The degree of hardening effected by hydrogenation depends largely upon the duration of the process, and by stopping the reaction at any given point products of varying consistence may be obtained. As the hydrogenation proceeds the iodine value steadily falls, until eventually a fat which has an iodine value of practically *nil* is produced.

The characteristic constituents in certain oils are also affected by hydrogenation. Thus, cotton-seed oil which has been converted into a solid fat no longer gives the distinctive colour reactions in Becchi's silver nitrate test, or in Halphen's reaction, but the sesamol in sesamé oil, which is the active agent in Baudouin's test, is not destroyed by hydrogenation. The insoluble bromide test for whale and other marine-animal oils is rendered uncertain, the proportion of bromides obtained decreasing with the progress of the reaction.

According to Leimdörfer there are distinct differences between the physical and chemical characteristics of hydrogenated and natural fats, whilst arachidic acid may still be isolated from hardened arachis oil.

Cholesterol and phytosterol are not greatly affected by hydrogenation at low temperatures, but after hydrogenation at 200° C. the cholesterol in animal oils and fats becomes resinified to a large extent.

Analytical Values of Hardened Oils.—The following results were given by hydrogenated fats prepared in Germany from whale oil for the manufacture of margarine :—

	Melting Point, °C.	Solidification Point, °C.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Molec. Equivalent of Fatty Acids.	Iodine Value.
Original whale oil .	fluid	fluid	9·50	192·7	0·27	287·7	144·8
Artificial tallow .	47·5	47·3	7·80	183·7	0·25	296·4	56·9
Hydrogenated whale oil . . .	41·9	31·9	5·30	190·9	0·18	282·0	57·8

Samples of completely hydrogenated oils examined by Mannich and Thiele give the following values :—

Hydrogenated Oil.	Melting Point, °C.	Iodine Value.	Saponification Value.	Melting Point of Insoluble Fatty Acids, °C.
Olive	70	0·2	190·9	71
Almond	72	0·0	191·8	71
Arachis	64	0·0	191·6	67
Sesamé	68·5	0·7	190·6	69·5
Cacao butter	64	0·0	193·9	65·5
Poppy-seed	70·5	0·3	191·3	71
Linseed	68	0·2	189·6	70·5
Tallow	62	0·1	197·7	64
Lard	64	1·0	196·8	62
Cod-liver	65	1·2	186·2	59

It will be readily understood from these figures that the presence of a hydrogenated oil greatly increases the difficulty of ascertaining the nature of a fat, and may even render the problem insoluble.

Uses of Hydrogenated Oils.—The early products of the hydrogenation process were used exclusively for technical purposes, such as soap-making and the manufacture of candles, and it was some time before edible hardened fats were prepared.

When the processes had been sufficiently simplified all kinds of oils were hardened, and used in the manufacture of margarine, artificial lard, and the like. For example, instead of using mixtures of oleostearin with cotton-seed or maize oils as the basis of margarine, these oils were hydrogenated either alone or in admixture with soft fats, such as coconut oil, until products of the required consistence were obtained.

At one time traces of nickel were invariably present in fats which had been hydrogenated with the aid of a nickel catalyst, and the results of various feeding experiments have been published to show that such traces are of no importance from a health point of view.

Moreover, steps are now taken to remove the nickel, by treatment with hydrochloric acid, or otherwise, from the hydrogenated products, and the metal is seldom present in the fats intended for food purposes.

It has been found by Klimont and Mayer that although hydrogenation removes the disagreeable odour of fish or whale oils there is a tendency for the odour to reappear after the fats have been kept for some time, and in their opinion this is the chief objection to the use of such hydrogenated oils in margarine.

CHAPTER V

BUTTER

Butter Fat.—The fat contained in suspension in the milk of mammals differs considerably in chemical composition from the body fat of the same animals. The latter consists mainly of glycerides of the higher fatty acids, notably stearic, palmitic, and oleic acids in varying proportions, whereas in the case of milk fats there is, in addition to compounds of these fatty acids, a large proportion of glycerides of volatile fatty acids.

It is upon this characteristic feature of butter fat that many of the methods of detecting foreign fats in butter are based.

A specimen of butter fat examined by Brown yielded 86·40 per cent. of insoluble fatty acids and 8·35 per cent. of soluble volatile fatty acids. The former included 32·85 per cent. of oleic acid, 1·83 per cent. of stearic acid, 38·61 per cent. of palmitic acid, 9·89 per cent. of myristic acid, and 2·57 per cent. of lauric acid. The soluble volatile acids were made up of 5·45 per cent. of butyric acid, 2·09 per cent. of caproic acid, 0·49 per cent. of caprylic acid, and 0·32 per cent. of capric acid.

The low proportion of stearic acid found was in accordance with the direct estimations made by Hehner and Mitchell, who obtained only small amounts in their examination of the fatty acids from a large number of samples of butter fat of different origin. It was interesting to note, that after the fatty acids had been exposed to the air for some weeks, there was apparently a gradual formation of stearic acid.

By the use of a modification of this method, however, Holland, Reed and Buckley (*J. Amer. Chem. Soc.*, 1916, xxi. 209) separated from 7 to 22 per cent. of stearic acid. They also found that the proportion of stearic acid in the insoluble fatty acids varied with the nature of the oil in the food of the cows.

The general composition of butter fat, as shown by the examination of Brown (*supra*), is as follows:—

Glycerides of—	Per Cent.
Dihydroxystearic acid	1·04
Oleic acid	33·95
Stearic acid	1·91
Palmitic acid	40·51
Myristic acid	10·44
Lauric acid	2·73
Capric acid	0·34
Caprylic acid	0·53
Caproic acid	2·32
Butyric acid	6·23

Naturally, different specimens of butter may show wide variations in the proportions of their different constituents, but the above may be taken as typical and as an illustration of the more complex character of milk fat than that of a body fat.

The glycerides in butter fat are probably present in the form of mixed glycerides, though, as yet, certain proof of this is wanting.

Butter.—Commercial butter consists of butter fat, water, casein, and salt, the proportion of fat usually ranging from about 84 to 87 per cent.

The following results obtained by Vieth (*Analyst*, 1891, xvi. 1) show the average composition to be expected :—

Butter.	Fat, per cent.	Curd, per cent.	Salt, per cent.	Water, per cent.
Danish (17 samples)	83·41	1·30	1·87	13·42
English (72 samples)	86·85	0·59	1·02	11·54
French (fresh, 108 samples) .	84·77	1·38	0·09	13·76
French (salted, 5 samples) . .	84·34	1·60	2·01	12·05
Kiel (4 samples)	85·24	1·17	1·35	12·24
Swedish (25 samples)	83·89	1·33	2·03	13·75

Water.—Statutory regulations are in force in many countries to limit the permissible amount of water in butter. In Great Britain and Ireland pure butter must not contain more than 16 per cent. of moisture, whilst the so-called " milk-blended butter " is not allowed to exceed the limit of 24 per cent.

The following limits are in force in other countries: *Belgium*, 18 per cent. unless declared; *Germany*, 18 per cent. for unsalted butter and 16 per cent. for salted butter; *United States*, 16 per cent.; *Canada*, 16 per cent.; *Queensland*, 16 per cent.; *Victoria*, 15 per cent.

These regulations have been found necessary, owing to the readiness with which a large excess of water (over 25 per cent.) may be churned into a butter without making it appear abnormally moist or interfering with its sale.

The effect of " salting " butter is to reduce the amount of moisture, as is shown in the results of Vieth, quoted in the table given above.

Richmond considers that the best proportion for a butter that is meant to keep well is 13·5 per cent.

Salt.—There is no regulation as to the amount of salt that may be added to butter, and the proportion will depend upon the popular taste; sometimes as much as 10 per cent. may be found.

Curd.—This term represents not only the solid nitrogenous substances derived from the casein of the milk, but also the milk sugar, etc., and its amount is roughly estimated by subtracting from 100 the percentages of butter fat, moisture, and ash which have been separately determined. The proportion thus found varies from a fraction of 1 per cent. to about 1·75 per cent., the average being a little over 1 per cent.

More accurate estimations of the true casein are obtained by determining the amount of nitrogen, and calculating the quantity of casein from the result.

Keeping Properties of Butter.—Rogers and Gray have studied the effect of the acidity of the cream upon the flavour of butter (U.S. Dept. Agricult., 1909, Bull. No. 119). They show that butter is liable to develop unpleasant flavours even when stored at temperatures as low as – 10° F., and that the amount of alteration increases with the acidity of the cream from which the butter was prepared.

No micro-organisms to which the more rapid deterioration of butter from very acid cream could be attributed were detected, nor did the changes appear to be due to the action of enzymes.

When the butter had been made from sterilised cream acidified with various acids there was a gradual development of unpleasant flavours, and this result indicated that the acid normally produced in milk by the lactic acid bacteria had an influence in bringing about slow decomposition of unstable compounds in the butter.

Butter made from sweet sterilised cream was found to show much less tendency to change on storage than that made in the ordinary way, but the flavour would as a rule be regarded as too insipid.

Flavours derived from the wood of the churn, or other external sources, would also be much more noticeable in the case of such butter than in that made from soured cream.

This lack of flavour has been shown by Storch to be due to absence of the products of certain bacteria which develop in the souring of the cream, and various species have been isolated, each imparting characteristic properties to the butter.

Thus Conn has demonstrated the practical advantages of inoculating the cream with cultures of specific bacteria, and has shown that in this way it is possible to give to the butter the particular flavours which previously had only been naturally produced at certain periods of the year. At the same time, butter thus artificially ripened was found to keep better and to retain its flavour longer than that prepared by the older method. This method of artificial inoculation with specific organisms has been successfully employed on a large scale in America.

Burr and Wolff (*Milchwirtschaftl. Zentralbl.*, 1910, vi. 241) have studied the effect of the parchment wrappings of butter upon the keeping qualities, and have found that under certain conditions parchment paper affords a suitable medium for the growth of moulds.

The main factors influencing this growth are a high percentage of moisture in the butter and the access of air. The presence of 1 to 1·5 per cent. of salt checks the growth, whereas unsalted butter is readily attacked.

A method of improving the keeping qualities of butter has been based upon the sterilising action of ultra-violet rays upon the water used for washing the butter in the dairy.

It has been pertinently pointed out by Dornic and Daire (*Comptes Rend.*, 1909, 149, 355) that it avails little to prepare butter from sterilised cream if the water used for washing it contain micro-organisms which tend to produce rancidity.

The apparatus employed by Dornic and Daire consists of a tank lined with glass, and provided with glass partitions over which the water passes, and receives the rays from two quartz electric lamps, which are inserted through holes in the cover of the tank.

About 3000 litres of water can thus be rendered practically sterile in a day, the number of bacteria being reduced by the treatment to an insignificant quantity.

The cream, or the butter itself, might be rendered sterile by this process, but an unpleasant flavour produced by the action of the ozone formed by the lamps prevents the method being successfully employed in practice.

A French patent has, however, been taken out (No. 400,921 of 1909) for sterilising butter or other fats in this way. The substance is spread in a thin layer upon an endless band or revolving drum, the movement of which carries it past a series of lamps emitting ultra-violet rays.

Rancidity of Butter.—There appears to be little doubt but that micro-organisms may play a part in the production of rancidity in butter, although the presence of light and air are probably the chief factors in the changes that take place.

Laxa, who studied the question with especial reference to butter (*Arch. Hyg.*, 1902, xli. 119), found that several mould fungi, and at least one bacillus (*B. fluorescens liquefaciens*), were capable of growing upon media containing butter fat and of breaking up the glycerides, with the liberation of free fatty acids, which were then in turn decomposed.

The acidity of the fat increases with the progress of the rancidity, but not necessarily proportionately, and a specimen of butter fat in which the oxidation products to which the rancid taste and odour are due may have a lower acid value than butter, which shows no trace of rancidity.

Many of the compounds produced in the development of rancidity are soluble, and may be separated from the fat by washing it with water. Advantage is taken of this fact in the preparation of "process" butter from stale or unsaleable genuine butter.

Issoglio's test (p. 52) might be applied to detect rancidity in butter, but, as a rule, reliance is mainly placed upon the taste.

Renovated Butter.—A product sold in large quantities under the name of renovated or "process" butter is prepared by melting down the fat of old butter, separating it from the curd and water, chilling it upon ice, and re-churning it with fresh milk and whey. By this means the casein is restored to the butter, and a mixture is obtained which answers to the chemical tests for fresh butter, but lacks its fresh flavour.

Several methods are employed for distinguishing process butter from the genuine product, the most satisfactory of which are based upon the physical alteration of the butter fat in the processes of melting and congealing. Thus, in the case of ordinary butter the separated fat when examined under the microscope, does not show the crystalline structure of the fat from renovated butter, and the difference is still more pronounced when the fats are compared in polarised light.

Other tests upon which a judgment may be based are the greater solubility of the "process" fat in glacial acetic acid (Cochran); and the appearance and behaviour of the separated curd, which is gelatinous when derived from fresh butter, and granular and flocculent when obtained from renovated butter, whilst a further distinction has been based on the ratio between the casein and the albumins.

Hess and Doolittle (*J. Amer. Chem. Soc.*, 1900, xxii. 150) also observed a difference in the behaviour of the two products when heated, genuine butter foaming, while process butter splutters in the same way as margarine, from which, however, it may be distinguished by other tests.

The trade in process butter is much more extensive in the United States than in this country, and numerous patents have been taken out to obtain a product which shall imitate ordinary butter still more closely.

Among them is the process claimed by Roos (U.S. Pat. 854,383, 1907). The fat separated from the old butter is melted and heated to a temperature of 108° to 110° F., and is then termed "butter oil."

About five parts of it are added to three parts of a previously churned mixture of acidified skimmed milk and fresh whole milk, and the whole stirred up until an emulsion is obtained. This is treated with cold water to cause crystallisation, and the resulting crystals are mixed with salt and exposed to the air for some time at the ordinary temperature, after which the mass is thoroughly kneaded to expel the salt and the excess of milk.

Preservatives in Butter.—Butter, which at one time was heavily salted, is now frequently preserved by the addition of a small amount of borax or other compound of boric acid.

The prevalence of the practice was shown by the evidence given by leading representatives of the butter industry before the Departmental Committee on Preservatives in Food (1901). One of these witnesses informed the Committee that his firm had ceased to use heat sterilisation of the cream, as it was found to impair the flavour of the butter.

It was further shown that the butter imported from Australia, Normandy, etc., contained 0·5 per cent. of boric acid; and that this amount was regarded by the trade as sufficient for the purpose.

In their report the Committee recommended that no preservative other than boric acid or borax, or mixtures of the two, should be permitted to be used in butter or margarine, and that the proportion should not exceed one-half per cent.

An attempt was made in France to prohibit absolutely the use of preservatives in butter, but the needs of the trade were too strong, and, as was mentioned above, the butter imported into this country from France is almost invariably preserved.

The presence of boron compounds is proved by melting the butter, separating the aqueous portion, rendering it faintly acid with hydrochloric acid, and immersing a strip of turmeric paper therein. On drying the paper at a gentle heat a purple-red coloration, changing to bluish black on the addition of ammonia solution, indicates the presence of boric acid.

Tests are sometimes applied for other preservatives, such as salicylic acid, sodium benzoate, sodium fluoride, and formalin, but these compounds are not of common occurrence in butter.

Some years ago butter intended for export to tropical countries was preserved by the addition of a fairly large proportion of glucose. This practice was most common in France.

Physical Characteristics.—Butter fat has a specific gravity ranging from about 0·907 to about 0·913 at 35° C., whereas the specific gravity of the animal fats used as adulterants is considerably higher.

It has been shown by Skalweit (*J. Soc. Chem. Ind.*, 1894, xiii. 54) that these differences are most pronounced at a temperature of 35° C., as is illustrated by the following table :—

Temperature, °C.	Lard.	Margarine.	Butter Fat.
35	0·9019	0·9017	0·9121
50	0·8923	0·8921	0·9017
60	0·8859	0·8857	0·8948
70	0·8795	0·8793	0·8879
80	0·8731	0·8729	0·8810
90	0·8668	0·8665	0·8741
100	0·8605	0·8601	0·8672

The specific gravity of coconut oil is also greater than that of animal fats.

Solubility.—Butter fat is considerably more soluble than animal body fats in various solvents, such as glacial acetic acid, alcohol, etc., and on this property have been based several rapid "sorting" tests for distinguishing between pure and adulterated butter.

One of these tests, known as the *Valenta test*, gives the temperature at which a solution of a definite quantity of the fat in a definite quantity of hot glacial acetic acid becomes turbid on cooling the liquid.

The following figures obtained by Chattaway, Pearmain, and Moor, show the difference between butter and margarine :—

	Maximum.	Minimum.	Mean.
Butter fat	39·0	29·0	36·0
Margarine	97·0	94·0	95·5

The natural variation in this respect between different samples of genuine butter is thus too great to permit of the detection of small quantities of margarine in butter.

Refractometric Examination.—The difference in the refractive power of butter fat and margarine is a valuable means of obtaining a preliminary idea as to the purity of a sample of butter, and several instruments have been specially constructed for the purpose. The most widely used of these is termed a *butyro-refractometer*, and it is readily possible by its means to distinguish in a few minutes between pure and grossly adulterated butter. Here again, however, the variations in the readings of samples of genuine butter of different origin are sometimes greater than between a sample of pure butter and one adulterated with a small percentage of margarine. Thus Crismer found that two pure samples of butter fat gave readings of 45·8 and 46, whilst two adulterated samples gave readings of 45·2 and 45·6 at 40° C.

The readings obtained by Thorpe (*J. Chem. Soc.*, 1904, lxxxv. 254), in the examination of 371 samples of English butter fat, ranged from 37·3 to 43·0 at 45° C., whilst readings of 42·0 to 47·6 have been recorded for the fat from Dutch butters.

Chemical Characteristics.—Owing to the large proportion of fatty acids of low molecular equivalent present in butter fat, the saponification value is naturally very high, ranging from about 219 to 240, though values both above and below these figures have been recorded for genuine butter.

Since coconut oil also has a high saponification value (254 to 260), mixtures of animal fat with that fat may readily be prepared which will give figures within the normal limits for butter fat.

The proportion of free fatty acids in freshly churned butter fat is very small (about 0·01 grm. per kilo. according to Duclaux), but it gradually increases as the butter is kept. A determination of the acid value may therefore afford some indication of the age of a sample of butter.

The iodine value of pure butter fat is usually between 25 and 40, but is liable to fluctuate considerably with the nature of the food given to the cows.

Of all the different so-called constants, the Hehner, Reichert and Polenske values, described below, are the most important as tests of purity, and an official method of determining the Reichert value has been established in this country, so as to eliminate errors due to variations in the size of the apparatus, duration of distillation, etc.

Hehner and Reichert Values.—The chief substances used in the adulteration of butter are beef fat and pig's fat (in the form of margarine), vegetable oils (also mainly in margarine), and (especially of late) coconut oil and palm-kernel oil.

The methods of distinguishing between butter fat and other animal fats are based upon the high proportion of soluble volatile acids in the former, and their practical absence from the latter.

Originally the test was devised by Hehner, who measured the amounts of insoluble fatty acids yielded by butter fat, and showed that they were very much less than those given by other fats.

It is now more usual, however, to employ the more rapid process devised by Reichert (with modifications by other chemists), in which the fatty acids are distilled under definite conditions which must be rigidly followed, and the proportion of them thus obtained is estimated by neutralisation with a standard solution of alkali. The details of the method are described at length in Chapter IX. The result is then expressed in the number of cubic centimetres of this standard alkali, and is termed the Reichert (or Reichert-Meissl) value of the fat.

The Reichert-Meissl value of pure butter fat has been found to vary under ordinary conditions from about 20 to 33, though figures far beyond either of these limits have been recorded in exceptional cases.

The values obtained by Thorpe (*J. Chem. Soc.*, 1904, lxxxv. 254), with 357 samples of English butter ranged from 22·5 to 32·6.

In calculating the amount of foreign fat in a butter from this value it is assumed as an arbitrary figure that an average butter fat has a Reichert-Meissl value of 28·78, and the percentage of added fat may thus be found approximately.

The difficulty, however, is that the values normally range so widely above and below this average, that it is quite possible to add 10 (or more) per cent. of foreign fat to a butter with a high Reichert-Meissl value, and still have a product giving a normal value.

On the other hand, cows frequently produce butter which gives a value far below the standard figure, and without special knowledge of the conditions to which this abnormality is due the butter may be condemned as adulterated with foreign fat.

This was shown in a striking manner a few years ago, when large quantities of butter imported into this country from Holland were condemned as adulterated on account of their low Reichert-Meissl values.

The causes of this abnormality were investigated by Van Rijn, who found that the mixed butter of a herd of cows might vary in its Reichert-Meissl value from 17·0 to 32·1.

The low figures were found to coincide with the end of the pasturage season, for after the cows had been stalled for a short time the butter became normal again. For example, the butter from a herd of seven cows had a Reichert-Meissl value of 24·4 on September 11, which had fallen to 19·0 on October 23. The animals were then taken from the fields, and their butter gave the following values: November 6, 21·5; November 20, 23·1; and December 11, 25·4.

This conclusion as to the effect of leaving the cows too late in the fields was borne out by the results of a Commission appointed to investigate the causes of abnormality of the butter produced in Belgium.

It was found that the butter giving such results was generally the product of small herds of cows; that its occurrence was most pronounced in the last four months of the year; and that with the return of spring the values became normal again.

The variations in this respect in English butters at different periods of the year are shown in the following results given by Thorpe (*loc. cit.*) :—

	May.	June.	July.	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	April.
Minimum	26·5	26·0	22·5	23·4	22·4	22·3	23·3	23·9	25·6	22·0	27·1	25·3
Maximum	32·8	32·8	31·4	30·5	29·5	29·6	32·9	30·4	31·0	31·6	34·3	33·1

It may be mentioned that in Belgium the sale of butter showing a lower Reichert-Meissl figure than 28 is prohibited by law, whilst in the United States the minimum value is fixed at 24.

Poor feeding has also an influence in lowering the Reichert-Meissl value, and to this cause must be attributed the low values frequently found in the case of Siberian butter.

Another factor influencing the degree of the Reichert-Meissl value is the time that has elapsed since calving. Thus it was shown by Kreit (*Analyst*, 1893, xviii. 134) that the values obtained at an early period of lactation were invariably higher, and that they then gradually fell. In some cases the butter from the milk of cows that had recently calved reached the high Reichert-Meissl value of 34·4.

This also affords the explanation of the occasionally low Reichert-Meissl values of Irish butter, which, as has been proved by Ball (*Analyst*, 1907, xxxii. 202), coincides with a period when the milk has been derived from cows at the very end of lactation. This period lasts for about six weeks, during which time the milk is richest in fat, while the fat shows the lowest Reichert-Meissl values. Thus the following results were obtained with butters churned on December 19, 1906:—

	Limerick.	Bruree.	Mallow.	Clonmel.	Tipperary.
Reichert-Meissl values .	22·7	21·5	23·3	23·5	22·1

The same abnormality does not occur in England, where the calving of the cows is distributed over the whole year, instead of, as in Ireland, taking place within six weeks of one another.

It is also possible that sufficient attention may not be given to the cows in Ireland, since the effect of feeding and good housing is to raise the Reichert-Meissl value of the butter, even in the case of cows at the end of their lactation period.

Influence of the Food of the Cows.—The results of numerous feeding experiments, in which quantities of different oils and fats were mixed with the daily fodder of the cows, have shown that the nature of the butter fat may be appreciably affected in this way. Thus Werenskiold (*Chem. Zentralbl.*, 1900, ii. 215) proved that cotton-seed oil could be detected in the fat from the milk of cows which had taken a small amount of cotton-seed oil-cake with their food, and this result was in agreement with the results of experiments carried out for the Board of Agriculture in this country (*Analyst*, 1898, xxiii. 255).

As a rule, however, the colour reaction indicating the presence of cotton-seed oil is very slight, and does not correspond to a proportion of more than 1 per cent.

In the analogous experiments of the Agricultural Board with sesamé oil-cake the butter from the cows did not give the characteristic colour reaction for that oil, even after they had been fed upon it for several weeks.

There is also evidence to show that the characteristic fatty acid of arachis oil does not pass into the milk of cows fed upon arachis-seed cake; but it has been shown by Paal and Amberger (*Zeit. Unters. Nahr. Genussm.*, 1909, xvii. 1) that feeding the animals upon copra may have some influence upon the composition of their milk fat, .and increase the proportion of insoluble volatile fatty acids.

Opinion is divided as to the advisability of having a fixed standard for a chemical property such as the Reichert value. Although such a limit as is fixed in Belgium excludes all doubt in condemning samples that fall below it, yet, as was found in the case of lard (p. 90), a fixed standard leads to an increase in the amount of petty adulteration, since it is not difficult for a skilful mixture to be made that will answer the requirements of a moderate standard.

In any case there is even now a systematic attempt to conform with what the adulterator presumes will be the standard by which the analyst will judge his product, and the present writer (S.) has frequently examined samples with a Reichert-Meissl value of 23 to 24 which in all probability contained a small quantity of foreign fat, but yet might conceivably have been genuine butter containing less than the average quantity of volatile fatty acids.

Nor does it follow that such butter is necessarily inferior as a food, for there is no proof that a slight deficiency in the amount of the glycerides of volatile fatty acids affects the nutritive value of the whole fat.

Coconut Oil in Butter.—The addition of coconut oil to butter, which has become increasingly prevalent of late years, has the effect of lowering the Reichert-Meissl value to a much smaller extent than the addition of animal fat.

This is due to the fact that coconut oil has itself a Reichert-Meissl value of 7 to 8, indicating the presence of a considerable amount of soluble volatile fatty acids, and it is therefore possible to prepare a mixture of animal fat, coconut oil, and fluid vegetable oil, which can be added to butter in a fairly large proportion without reducing the Reichert-Meissl value of the latter below 24 or 25.

The problem of detecting coconut oil in butter has therefore received much attention of late, and numerous methods have been devised for estimating the amount of such addition.

Speaking generally, these are based upon the fact that coconut oil contains a high percentage of lauric acid (up to about 45 per cent.), whereas that acid is only present in very small proportion in butter fat.

Now, since lauric acid will volatilise in a current of steam, but, unlike the lower fatty acids (butyric, caproic, caprylic, and capric acids), is not soluble in water, it is possible to obtain a measure of its proportion by continuing the distillation as in the Reichert-Meissl process until the whole of the volatile fatty acids (soluble and insoluble) have passed over. The distillate, when filtered, is separated into two portions—soluble and insoluble—and the latter may be dissolved in alcohol and its acidity determined by titration with standard alkali solution.

The Polenske Value.—The proportion of the volatile insoluble fatty acids obtained under specified conditions, which must be rigidly adhered to, is known as the "Polenske value," and enables an estimate to be formed of the amount of coconut or palm-kernel oil in butter or margarine. The details of the method are described in Chapter IX.

Another method devised by Blichfeldt (*J. Soc. Chem. Ind.*, 1910, xxix. 792), is based on the determination of the proportion of total volatile fatty acids, and of the soluble and insoluble silver salts yielded by them, the results being expressed in equivalent values. The following results are typical of those obtained by this method :—

	Total Volatile Fatty Acids.	Soluble Silver Salts.	Insoluble Silver Salts.
Butter	32	29	3
Coconut oil	20	14	16
Palm-kernel oil . . .	15	3	12

In Shrewsbury and Knapp's method (*Analyst*, 1910, xxxv. 385), advantage is taken of the fact that lauric acid, the predominating fatty acid in coconut oil, is readily soluble in dilute alcohol, and that the amount of standard alkali required to neutralise the solution will afford a measure of that acid.

When thus examined under comparable conditions coconut oil gave a value of 163, whilst various samples of butter fat gave results ranging from 23·6 to 31·2. It was found in experimental estimations that the proportion of coconut oil in mixtures of that fat with butter, calculated from the results of this method was about 5 per cent. too high.

Another method for the detection and approximate estimation of coconut and palm-kernel oils and butter has been based by Burnett and Revis (*Analyst*, 1913, xxxviii. 255) upon the degree of solubility of the barium salts of the insoluble volatile fatty acids, in alcohol of a definite strength. The temperature at which the solution of the barium salts prepared under specified conditions, becomes turbid, is noted.

Artificial Colouring Matters.—The nature of the food given to the cows, their breed, and the season of the year, all have an influence upon the colour of the butter; that produced in summer, for instance, being more yellow than that produced later in the year.

When exposed to the action of air and light the natural colour of butter gradually fades, and ultimately the fat becomes colourless.

The popular demand for a butter of pronounced yellow colour—a demand inspired by the belief that intensity of colour indicates purity—has led to the artificial colouring of pale butter.

The colouring matters employed for this purpose include that of the carrot, annatto, turmeric, saffron, marigold, and various aniline dye-stuffs.

Special azo dye-stuffs, soluble in oil, are frequently used, especially in the United States. They may be detected by mixing a little fuller's earth with the butter-fat which has been separated from the curd, the earth assuming a pink or light red coloration in the presence of such dyes.

Since in the United States the sale of margarine containing artificial colouring matters is prohibited, the desired yellow colour is now frequently obtained by the use of palm oil, mustard-seed oil, and similar fats of intense colour. Special tests have therefore been devised for the detection of these fats in butter.

CHAPTER VI

LARD

Rendering of Lard.—Lard may be defined as the fat separated for use as food from the adipose tissue of the pig.

In the process of rendering lard the tissue is first finely divided or minced in a machine, or is crushed between rollers, and is then heated either by dry heat or by means of steam to expel the fat from the ruptured fat-cells.

A product of excellent quality is obtained by subjecting the mass to dry heat at a temperature just sufficient to melt the fat; and a process of this kind is frequently used in the preparation of the fat for margarine.

At higher temperatures some decomposition of nitrogenous compounds in the adipose tissue takes place, and special means must be provided for carrying off the obnoxious vapours thus produced.

The use of steam in a steam-jacketed pan or digester enables the temperature to be regulated with greater nicety, and prevents the fat being overheated and acquiring a burnt flavour.

A more rapid process of rendering lard is to heat the finely divided material with water in a suitable vessel and subsequently to skim off the fat that rises to the surface. At first the temperature is kept as low as possible in order to separate the portions of the fat of lowest melting-point. Then the temperature is raised, with the result that a fat of greater consistence rises to the surface; and finally the water is brought to the boiling-point to separate, as far as is possible by this means, the residual fat. In this way a fractionation of the lard takes place.

A process more frequently employed than the preceding one is that in which the adipose tissue is rendered, in a closed vessel or digester, capable of resisting the action of steam introduced under pressure.

Numerous patents for apparatus embodying this principle have been taken out, especially in the United States, various modifications of the mode of heating, separation of the fat, and filtration being claimed.

In some of the largest works in Chicago and other centres of the American lard industry a great number of such digesters is employed, some of them having a capacity of upwards of 20,000 gallons. Each of these vessels is reserved for its particular kind of fat, so as to facilitate the speed of working.

In a typical digester the finely minced fatty matter, which has been separated from the recently killed animal, is introduced from above through a man-hole, which is then screwed down hermetically. Within the digester is a perforated false bottom upon which the material rests, and beneath this is a perforated steam coil, connected by means of a pipe with an outside boiler, from which steam is admitted until a pressure of about four atmospheres is shown upon the gauge. Condensed water is drawn off through a cock near the bottom of the vessel, while a similar cock is provided near the top for testing whether the fat is being liberated. After a digestion of about twelve hours the steam supply is shut off, and the pressure in the digester reduced by opening the safety valve. Then, after standing for some time for separation to take place, the aqueous layer is drawn off through taps arranged at different levels near the bottom. The rendered fat, which has separated on the surface as a melted layer, is next withdrawn, and finally the residual mass is expelled through an outlet in the bottom, which can be controlled from above by a rod passing through the body of the apparatus.

Commercial Grades—In the United States (which probably produces more lard than the rest of the world put together) various grades of lard are recognised, depending mainly upon the part of the animal whence they were derived. Thus, according to Wiley (U.S. Dept. Agriculture, Bull. 13), the following descriptions of lard are known in the trade :—

(1) *Neutral lard*, which is the product of the absolutely fresh leaf of the hog, rendered at a temperature between 105° and 120° F. It is chiefly used in the manufacture of margarine.

(2) *Leaf lard*, prepared from the residue left after removal of neutral lard at a lower temperature.

(3) *Choice steam lard*, or *Choice lard*, obtained from the residual tissue from neutral lard and from adipose tissue from the back of the animal.

(4) *Prime steam lard*, which may be the product of any part of the animal, and especially of the fatty tissue from the head, heart, and intestines.

(5) *Guts*, a low grade of lard rendered from scraps from any part of the animal, with the exception of the heart and lungs.

In addition to these, still lower grades of pigs' fat, which are used for soap and other technical purposes, are separated from hogs that have died on their way to the slaughter-houses, or from refuse material. These include *white*, *brown*, and *yellow grease*, and *pigs' foot grease.*

More recent definitions, issued by the Chicago Board of Trade, include the following grades :—

(1) *Neutral lard No.* 1, which consists of the leaf fat rendered below 50° C.

(2) *Neutral lard No.* 2, derived from the back fat.

(3) *Leaf lard*, obtained by digesting the residue from (1) with high-pressure steam.

(4) *Choice kettle-rendered lard*, obtained from the residue from (2).

(5) *Prime steam lard*, rendered from trimmings and fatty tissues from other parts of the animal by means of high-pressure steam.

Greases of various grades are obtained from the intestines and viscera.

The product known in Germany as *pure lard* is obtained by a process of steam-rendering, followed by mechanical agitation of the separated fat in a closed vessel until it begins to solidify. An addition of a small proportion of a more solid lard is then made, or, in the best grades, a small proportion of lard stearin is added. According to Voigtländer (*Zeit. angew. Chem.*, 1898, 857), this treatment, which is known as the Hungarian process, prevents the lard becoming fluid on keeping.

American lard, even when free from any addition of vegetable oil, is often of a more fluid character than European lard, this being due partly to differences inherent in the hogs and partly to the influence of the food given to the animals.

Composition.—Lard, like most natural products, shows wide variations in its chemical and physical characteristics, and this increases the difficulty of basing definite conclusions as to purity on the results of analyses. Even in the case of the same animal wide variations are observed in the composition of fat taken from different parts of the body, as is shown below.

Chemically considered, lard may be said to consist of glycerides of stearic, palmitic, lauric, and myristic acids, and of the liquid fatty acids, oleic and linolic acids; and the different physical properties of different samples of lard are due, in the main, to variations in the proportions of these different constituents. For instance, the firm fat from the leaf or kidneys of the animal contains fatty acids with a high percentage (about 15 per cent.) of stearic acid, and a low percentage (about 58 per cent.) of oleic acid; whereas the fat from the neck and back, which is very soft, contains fatty acids with about 9 per cent. of stearic acid, and about 75 per cent. of oleic acid.

Lard Crystals.—A curious property of lard, upon which reliance has often been placed as a test of purity, is that when it is dissolved in ether and the solution is gradually allowed to evaporate, crystals of characteristic form are often produced.

The fat crystals from an ordinary soft lard have flat edges and chisel-shaped ends, whereas the similar crystals from beef fat are in the form of bunches of needle-shaped crystals. A small proportion of beef fat added to a soft lard influences the crystallisation sufficiently to produce bunches of needle-shaped crystals, though chisel-ended crystals may also be detected.

Unfortunately for the purpose of this test, flare or leaf lard may also produce crystals which very closely resemble those derived from beef fat, and this resemblance is rendered closer by re-crystallisation, so much so that in some cases the two kinds of crystals are practically indistinguishable.

Hehner and the writer (Mitchell) found that the needle-shaped crystals contained a higher proportion of stearic acid than the chisel-ended crystals, and attributed the characteristic differences to this fact. It has been shown, however, by Kreis and Hafner that the difference is due to the characteristic flat crystals of lard consisting of a definite mixed glyceride, whereas the crystals from beef and mutton fat consist of another mixed glyceride, palmito-distearin.

According to Dunlop, it is possible, by continued re-crystallisation of beef-fat crystals, to obtain eventually a deposit containing crystals which are practically indistinguishable from those given by an ordinary lard.

From all this it will be seen that there is considerable risk of making a mistake, if judgment of the purity of lard be based solely upon the form of the crystals, as has sometimes been done. The fact that the crystals are chisel-shaped may be regarded as presumptive evidence of the purity of a lard, but the occurrence of bunches of needle-shaped crystals does not necessarily indicate an addition of beef fat.

Polenske's Method.—It was found by Polenske that the difference between the melting and solidification points ("the difference value") was fairly constant for a particular lard, but often differed considerably from the values shown by other fats. For example, lard gave difference values of 19 to 21 (in degrees Centigrade), whereas beef fat showed values of 12·8 to 14·7, and butter fat values of 11·7 to 14·3.

Experiments made by Bömer and Limprich (*Zeit. Nahr.*

Genussm., 1913, xxv. 367) have shown that these "difference values" depend upon the presence of different glycerides in the fats. Lard contains a mixed glyceride—which from its assumed molecular structure is termed α-palmito-distearin. An isomeric glyceride is also present in beef and mutton fats, and this from its structure is termed β-palmito-distearin. The former has a difference value of 18·4, whilst the glyceride of beef and mutton fats has a value of 11·8. In Bömer's experience the method may be made capable of detecting about 20 per cent. of beef fat and 15 per cent. of mutton fat in lard.

Bömer's Method.—An analogous melting-point method has been based by Bömer (*Zeit. Untersuch. Nahr. Genussm.*, 1913, xxvi. 559; 1914, xxvii. 153) upon the fact that the distinctive glyceride of lard has a melting-point which differs by 5·2° C. from the melting-point of its separated fatty acids, whereas in the case of the corresponding glyceride of beef and mutton fats the difference is only 0·1° C.

This method appears to be capable of detecting about 5 per cent. of beef or mutton fat in lard.

Influence of Food.—A point of considerable importance to the manufacturer of lard is that the food given to the animal may have a pronounced influence upon the composition and chemical reactions of the lard.

The fat of the wild boar differs from that of the domestic hog in being of a much more fluid nature. There is also some difference between the fat of wild and domestic hogs, the former containing a greater amount of unsaturated glycerides.

The more fluid character of American lards as compared with European products is to be attributed, in part at all events, to the animals being fed upon cotton-seed cake.

It has been shown by Dunlop, however (*J. Soc. Chem. Ind.*, 1906, xxv. 459), that hogs fed upon cotton-seed cake give lard yielding pronounced colour reactions for cotton-seed oil, but not, judging by the iodine value, containing an abnormal amount of fluid fatty acids.

Animals fed upon coconut-oil cake (copra) also show the influence of the food in their lard, which, without special knowledge of this fact, would certainly be condemned as having been adulterated with that vegetable fat.

This is shown in the following analytical values of lards from Philippine hogs to which a daily supply of coconut-oil cake had been given (Gibbs and Agcaoili, *Philippine J. Science*, 1910, v. 33) :—

Lard.	Refractometer reading at 40° C.	Saponification Value.	Iodine Value.	Iodine Value of Fatty Acids.	Melting-point of Fatty Acids, °C.
From maize-fed hogs :—					
Maximum . . .	46·0	199·0	52·7	53·8	43·8
Minimum . . .	42·5	196·0	46·7	50·0	41·6
Mean . . .	44·7	196·9	49·4	51·7	42·7
From copra-fed hogs :—					
Maximum . . .	47·0	213·7	42·5	46·2	42·3
Minimum . . .	44·0	204·6	32·5	36·2	39·4
Mean . . .	45·3	208·9	37·7	41·3	40·4

Lard derived from pigs which have been fed with abnormal quantities of coconut, maize, sesamé, and cotton-seed cakes will contain a smaller amount of the distinctive lard glyceride, α-palmito-distearin, than ordinary lard, but the variation thus caused is not sufficient to interfere with the detection of beef fat by Bömer's method (*supra*).

The phytosterol contained in vegetable fats does not pass into the lard of pigs fed upon cotton-seed meal, and the phytosteryl acetate test for vegetable oils is, therefore, not affected by the food given to the animals.

Acidity of Lard.—In order to obtain a practically neutral product, the fat intended for lard should be rendered as soon as possible after the animal has been killed. After standing for some time, the fat in the adispose tissue gradually undergoes decomposition, with the liberation of free fatty acids, and the acidity steadily rises. In refined lard the process of hydrolysis is greatly checked through the removal of nitrogenous substances, but the development of acidity will continue when the fat is exposed to the influence of light and air.

As a rule, a freshly prepared lard does not contain more than 0·5 per cent. of free fatty acids (as oleic acid), and frequently the proportion is very much lower. Thus the acidity of fats from the leaf and kidneys of six Philippine hogs examined by Gibbs and Agcaoili (*loc. cit.*) ranged from 0·28 to 0·38 per cent. On the other hand, the intestinal fat contained considerably more free fatty acids (0·86 per cent.). Samples of American lards examined by Wiley (*loc. cit.*) had an acidity ranging from 0·35 to 1·0 per cent. An acidity in excess of 1 per cent. probably indicates either that the lard was not prepared from fresh material or that it has been exposed to the air for some time.

Water.—Lard should not contain more than a small proportion (0·75 per cent. at most) of water, and as a rule most commercial samples contain considerably less than 0·5 per cent.

Polenske (*Arb. a. d. Kaiser. Gesundheitsamte*, 1907, xxv. 505) found that there was a relationship between the temperature at which the melted fat became turbid on cooling and the proportion of water present, and on this fact based a rapid method of estimating the moisture. Thus the following figures were obtained by Fischer and Schellens (*Zeit. Unters. Nahr. Genussm.*, 1908, xvi. 161):—

Water per cent. .	0·45	0·40	0·35	0·30	0·25	0·20	0·15
Turbidity Temperature °C. . .	95·2	90·8	85·0	75·8	64·6	53·2	41·2

In their opinion, based upon the examination of a large number of German lards, the proportion of water should be less than 0·3 per cent., corresponding to a turbidity temperature not exceeding 75° C.

Gross adulteration of lard with water is no longer a common practice.

The Iodine Value.—Important information as to the purity of lard is sometimes afforded by a determination of the percentage of iodine with which it will combine.

As a rule, European lards have iodine values not exceeding 61, and an iodine value considerably in excess of that figure, say 66, suggests the addition of cotton-seed oil or of other vegetable oils with high iodine values.

From what has been stated above, however, it will be seen that an abnormal iodine value is not in itself sufficient proof of adulteration, since American lards of genuine character may show that characteristic.

The differences in this respect between American and German lards are attributed by Voigtländer (*loc. cit.*) to the fact that American lards contain a large proportion of lard oil of a more unsaturated character. Thus, while German lard contains only about 50 per cent. of lard oil with an iodine value of 70–75, American lard may contain about 60 per cent. of lard oil with an iodine value of 88.

Some of the semi-fluid Russian lards sold in Germany contain as much as 90 per cent. of lard oil.

Of 100 samples of American lard imported into Germany, 88·5 per cent. had an iodine value between 61 and 66, and 41 per cent. a value exceeding 64.

The fixing of a standard for the iodine value of lard is unlikely to result in the sale of a purer product, judging by the experience of places where such a standard has been fixed. Thus at one time 62 was fixed as the limit for the iodine value in Bavaria, and the result was a widespread addition of beef stearine to make the lards answer to this requirement.

Lard Oil.—The fluid portion expressed from lard in the separation of lard stearine is known as *lard oil.*

It has a soft, pleasant taste, and, being almost free from odour, forms a good edible oil.

It consists in the main of olein, with a little linolin and a small proportion of glycerides of solid fatty acids, chiefly palmitic acid. A typical sample will have values similar to the following :—

Sp. gr. at 15.5° C.	Saponification Value.	Hehner Value.	Iodine Value.	Solidification point.	Melting-point of Fatty Acids.
0·914	194	97	76	− 4° C. to + 10° C.	35° C.

It is thus evident that a large amount of lard oil can be added to olive oil without making the values of the mixture abnormal.

It also gives a similar product in the elaidin test, and the phytosterol test (p. 132) is probably the best means of detecting it.

In turn it is liable to be adulterated with cheaper vegetable oils, such as arachis, cotton-seed, and sesamé oils, the presence of each of which would be shown by their special tests. The oleo-refractometer is also a means of determining the purity, since the ordinary reading of lard oil, which ranges from about − 1° to − 5°, would be increased by most of the oils employed as adulterants (with the exception of other animal oils and arachis oil).

CHAPTER VII

MARGARINE AND OTHER BUTTER SUBSTITUTES

Margarine, Oleomargarine, or Artificial Butter—Invention and Development—Modern Processes and Formulæ—Machinery—Use of Hydrogenated Oils—Vegetable Butter.

It has already been pointed out in Chapter I how essential is a fair proportion of fat in the human diet, and, prior to the introduction of artificial butter, this could only be largely made up among the poorer classes of the community by the use of "dripping," the price of genuine butter being prohibitive. Realising the importance of the subject, the French Government in 1869 offered a prize for the discovery of an artificial substitute for butter, which should not only be cheaper, but also remain free from rancidity for a longer period than butter. This led Mège-Mouries, a French chemist, to investigate the whole question of the formation of fat in milk, and he was successful in securing the prize. Physiological experiments soon led him to the conclusion that in the series of transformations by which the butter fat is produced in the animal economy, the carbohydrate matter consumed by the animal is first converted into fat, and this in turn, after being deprived of much of the stearin it contains, by respiratory combustion, is changed by the digestive action of pepsin into butter fat, and a method was devised for effecting this latter process artificially.

The original plan adopted by Mège-Mouries was to take 1000 kilos. of fresh beef fat, preferably from the kidney or intestines, and after thoroughly comminuting it and freeing it from tissue, to warm it at 45° C. with 300 kilos. of water, 1 kilo. of sodium carbonate, and two sheep's or pigs' stomachs for two hours, when, under the action of the pepsin, the fat separated completely from any remaining tissue, and came to the surface as a homogeneous fluid. This was then decanted into a second vessel, warmed to 45° C., and washed with a 2 per cent. solution of common salt, which prevented any fermentation. After allowing it to stand, a limpid yellow fat separated, having a butter-like odour, and on cooling to 20–25° C. this crystallised to a semi-solid mass, with a granular structure which, when the fat was cut in thicknesses of half an inch, wrapped in linen cloths, and subjected to a moderate hydraulic pressure between hot plates, at a temperature of 25° C., allowed 50 to 60 per cent. of a soft fat, comparatively free from stearine, to be expressed.

This fluid fat, or "oleomargarine," as it was called, solidified on cooling, and constituted what was originally sold in Paris under the name of "Margarine."

This soft fat was next converted by Mège-Mouries into a product more closely resembling natural butter by churning it for two hours with 10 per cent. of cow's milk, and water in which was macerated 0·4 per cent. of cow's udder, complete emulsification being effected by the action of the pepsin and the churning. After washing with cold water, salting, colouring with annatto, and finishing off as with ordinary butter, a very good imitation of the natural article was obtained.

According to Boudet, artificial butter thus prepared has a melting-point of 17 to 20° C., contains about 12·5 per cent. of water, and, in the dry state, 1·20 per cent. of insoluble casein, and is less liable to become rancid than natural tallow.

Factories were soon erected at Poissy and at Liesing, near Vienna, to work the process, which was patented by Hippolyte Mège, in England, in 1873. The English patent claimed a process for preparing artificial butter by mixing the oleomargarine with water containing sodium bicarbonate, casein, and mammary tissue. The sale of artificial butter was authorised by the Council of Hygiene of Paris in 1872, the use of the name "butter" to describe it being prohibited.

The name "margarine" was first applied by Chevreul to what was at that time considered to be a definite single compound of margaric acid with glycerin, and to occur in human fat and olive oil. Subsequent research by Heinz has shown, however, that this so-called margaric acid was in reality a mixture of stearic and palmitic acids, and the term "margarine," therefore, did not represent a definite chemical body. The name "oleomargarine" was introduced to signify what was believed to be a mixture of olein and margarine from which the stearin had been separated. Part of the "margarine" is now known to consist of stearin and palmitin, so that the oleomargarine still contains these two glycerides, though to a much smaller extent than in the original beef or mutton fat. The softer fat, from which the stearine has been removed, is known in America as "oleo oil," the artificial butter made therefrom being termed "oleomargarine." In this country it was decreed by the Margarine Act of 1887 that all artificial butter should be sold under the name of "margarine," and this has long since become a well-established, popular name, such terms as "butterine," and "Dutch butter," which had gradually come into use, being declared illegal by this Act.

The successful working of the Mège-Mouries process soon led a number of other investigators to take up the subject of the production of artificial butter, and the next few years were prolific in patents for the purpose.

Among many others, Lake, in 1871, patented the admixture of cotton-seed oil; E. G. Brewer, in 1874, the churning of treated tallow with 3 to 4 per cent. of sour milk and 2 per cent. of oil; and Pitt, in 1877, the addition of arachis oil; Mège Mouries the same year obtaining a further patent for the use of an artificial gastric juice, consisting of hydrochloric acid and acid calcium phosphate, to help in the artificial digestion of the fat.

In spite of these improvements, the method of margarine manufacture does not appear to have undergone much change prior to the discovery of the methods of hydrogenating oils; and the original type of margarine is to-day in most respects closely similar to that originally proposed by Mège Mouries, with the exception that the artificial digestion of the fat is now dispensed with, and a certain proportion of vegetable oils is generally added.

In this country the oleomargarine, or basis of artificial butter, consists usually of the softer portion of tallow or "premier jus," but in America a very large part of this, which after further treatment is there known as "oleo oil," is replaced by "neutral lard" obtained from the perfectly fresh leaf, or kidney and bowel, fat of the pig. The preparation of the "neutral lard" is almost identical with that adopted for tallow, and as the latter is largely employed in this country, the modern preparation of margarine with this as a basis will now be described.

Modern Processes.—The carefully selected caul fat of freshly killed oxen is first washed in a vat with warm water to remove blood and tissue, then hardened by chilling with ice water, and thoroughly comminuted by passage through rollers or cutting machines. It is next transferred to tin-lined and steam-jacketed vessels, in which it is raised to a temperature of about 40 to 45° C., when the softer portions of the tallow melt and rise to the surface, the separation being facilitated by sprinkling salt over the surface.

This clear oil, which is known as "premier jus," is then siphoned off into a second series of steam-jacketed vessels, in which it is heated to about 45° C., after which more salt is added, and a further settling takes place. The clear, supernatant oil is next transferred to shallow wooden vats, in which it is allowed to stand for three to five days at a temperature not exceeding 20° C., in order to crystallise out the stearine, after which it is thoroughly mixed, wrapped in canvas cloths, and subjected to pressure, whereby the soft "oleo oil," or oleomargarine, is separated from the harder stearine or oleo-stearine, which is used in the manufacture of lard substitutes, or sometimes in margarine in place of part of the oleomargarine, when a large quantity of vegetable oils has been employed.

The oleo oil is then removed to churns, in which it is mixed with "neutral lard," cotton-seed oil, olive oil, sesamé oil, maize oil, or other vegetable oil, and milk (fresh or sour) or cream, or sometimes water, a certain proportion of butter being frequently added to impart a better flavour to the margarine.

Emulsifying Machinery.—Several types of machines are in use for effecting an intimate admixture of the fat and milk, etc. One of these, which is known as the *margarine churn*, is a cylindrical vessel which contains rotating agitators, and inlets for the introduction of water or steam. After the milk has been heated to about 25° to 35° C., the melted fat, or mixture of fats, is gradually admitted, and the agitation continued until an emulsion is produced. The mixture is now cooled by the admission of cold water until it nearly solidifies, and is then run out to be cooled.

Schroeder's Emulsifier, which was patented in 1905 (Eng. Pat. 25,404), is an improvement on the old margarine churn. The emulsifying vessel is much smaller, and has two agitators which beat the mixture into a fine emulsion, while revolving at a high speed. After being discharged from this vessel, the emulsion is subdivided into a still finer cream in another apparatus, and is then passed through the cooling apparatus; or in some cases, where a battery of such churns is used, the mixture is run directly into tubs without previous cooling.

Silkeborg's Emulsifier.—A different type of emulsifier was patented in 1914 by Silkeborg (Eng. Pat. 4659). It is in the form of a hollow cylinder with a central shaft carrying the agitators, and is provided with a heating jacket. The mixture of fat and milk is driven by the rotating blades against perforated baffle plates, the holes in which effect the fine subdivision of the emulsion.

Blichfeldt's Emulsifier (Eng. Pat. 18,048, 1914) contains a perforated disc which rotates on a shaft near the side of the vessel. The milk is introduced through openings in the hollow shaft, while the melted fat is admitted through a separate pipe.

Cooling Machinery.—In order to effect rapid cooling of the emulsified mixture, either the so-called wet or dry method may be used. In the former method either ice-water or water chilled by a refrigerator is used as the cooling agent. For example, in one form of apparatus a thin film of the emulsion is delivered on to a sloping trough, where it meets a current of cold water, and falls in a solidified mass into a receiver.

In another type of apparatus the emulsion is discharged in a fine stream on to a drum which revolves in cold water, and the solidified mass removed from the surface by means of a scraper and delivered on to a travelling band. In some factories skim-milk or butter-milk is used as the cooling agent.

Fats, such as coconut oil and palm-kernel oil, are liable to become crystalline when cooled by this wet method, and in such cases chilled air is sometimes used as the cooling agent, as, for example, in the process claimed in Eng. Pat. 20,292, 1911).

In *Christensen* and *Lauridsen's* cooling machine (Eng. Pat. 20,568, 1912) the cooling is effected by means of a current of chilled brine, which circulates through the interior of a cylinder. The solidified emulsion is then removed from the exterior surface of the rotating cylinder by means of a fixed scraper.

A similar principle is used in *Jurgen's* machine (Eng. Pat. 100,863, 1914), in which a cylinder, through which circulates water at the same temperature as the emulsion, revolves partly in the mixture, and at each revolution transfers a certain quantity of the material to the cooling cylinder. After being cooled the so-called "crystals" are delivered to a special vessel, in which they are left for some hours to promote the action of the bacteria introduced with the milk. Finally they are mechanically kneaded to give the mass the consistence of butter and remove the excess of water.

The following analyses, given by Clayton (*J. Soc. Chem. Ind.*, 1917, xxxvi. 1208), show the composition of the crystals from two churnings of 100 gallons of soured milk, with one ton of oils containing animal fat, before and after being rolled :—

	Fat, per cent.		Water, per cent.	
	1.	2.	1.	2.
Crystals	67·30	67·30	27·46	27·47
Rolled product . . .	78·38	80·23	16·03	12·47

On the average the crystals contain about 33 per cent. of water, and the rolled product 14·5 per cent., the statutory limit for margarine being 16 per cent. Additions of salt, colouring matter, preservatives, etc., are made by means of "blenders," which are mixing machines provided with curved revolving blades. The addition of butter in an amount not exceeding 10 per cent. is permissible as a flavouring agent, and boric acid (up to 0·5 per cent.) is often used as a preservative.

Older Formulæ.—The number of materials available renders a very large variety of combinations possible, and, naturally, successful formulæ used by private firms are kept secret. The following formulæ were published, however, by the United States Census Report for 1900 :—

CHEAP GRADE.

Oleo oil	495 parts
Neutral lard	265 ,,
Cotton-seed oil	315 ,,
Milk	255 ,,
Salt	120 ,,
Colouring matter	1¼ ,,

which is sufficient to produce 1265 to 1300 parts.

MEDIUM HIGH GRADE.

Oleo oil	315	parts
Neutral lard	500	,,
Cotton-seed oil	280	,,
Milk	280	,,
Salt	120	,,
Colouring matter	1½	,,

producing 1050 to 1080 parts.

HIGH GRADE.

Oleo oil	100	parts
Neutral lard	130	,,
Butter	95	,,
Salt	32	,,
Colouring matter	½	,,

producing about 325 parts.

Such a formula as this would not be permissible in this country, where the maximum addition of butter to margarine is fixed by law at 10 per cent., and the neutral lard is more usually replaced over here by oleomargarine or "oleo oil," a suitable formula being as follows:–

Oleomargarine	230	parts
Cotton-seed oil	40	,,
Olive oil	20	,,
Butter	30	,,
Salt	32	,,
Colouring matter	½	,,

The proportion of cotton-seed oil should not, speaking generally, exceed more than about 25 per cent., or its characteristic flavour becomes apparent. Besides cotton-seed and olive oils, arachis, palm-kernel, and coconut oils now enter frequently into the composition of margarine, and in Germany the use of sesamé oil to the extent of 10 per cent. has been compulsory since 1897. Palm oil, which imparts a yellow tint to the margarine, is also occasionally incorporated. This being a firm fat enables the proportion of animal fat to be reduced.

The colouring matter usually employed is annatto, but turmeric and saffron are also occasionally used. The use of mineral colours is most objectionable, and coal-tar colouring matters are to be discouraged, though azo dyes are occasionally met with.

Glycerin is sometimes added to margarine to impart a glossy appearance, and sugar or glucose to sweeten it or improve its texture, though this is said to injure its keeping qualities.

Hydrogenated Oils in Margarine.—The solution of the problem of converting liquid oils into solid fats by hydrogenation has led to great changes in the manufacture of margarine. Instead of having to use a mixture of oils and fats in the suitable proportion to give a product of the required consistency, the manufacturer can now make use of a mixture of soft fats and oils, or even of a single oil, which he hardens to the desired extent. A further advantage is that deodorisation of the fat is simultaneously effected in the process.

In some cases oils which have thus been hardened are mixed with natural oils and fats, but in the opinion of Ellis (*J. Soc. Chem. Ind.*, 1912, xxxi. 1165) it is preferable to use only one oil, which is hydrogenated into a solid fat.

In certain continental factories fish and whale oils, deodorised and hardened by hydrogenation, are used for margarine, but Klimont and Mayer (*Zeit. angew. Chem.*, 1914, xxvii. 645) have found that although otherwise suitable for this purpose, the original odour of such oils is liable to reappear after some time. They have based a test for hydrogenated fish oils upon the amount of crystals formed when the fat is dissolved in acetone and allowed to stand.

Many methods have been devised for causing margarine to froth and become brown when heated, as does genuine butter. The addition of a fair proportion of butter will, of course, secure this, but in the absence of butter it may be accomplished by adding a sufficient quantity of milk. The introduction of casein, lecithin, or cholesterol has been suggested for the purpose, and Fendler has patented the use of 0·5 per cent. of egg yolk, whilst subsequent patentees have claimed the preliminary emulsification of the egg yolk with salt solution, lactic acid, etc. Mitscherlich patented the addition of meat extract or yeast, for the same purpose.

Though not really necessary in a properly made margarine, various artificial flavourings are occasionally added, ostensibly to render the flavour more similar to that of genuine butter, but more probably, in many cases, to enable a proportion of the margarine to be used in the adulteration of butter without detection by the usual chemical methods. Such flavouring materials include butyric acid or other volatile fatty acids, and certain butyrates, these being dissolved in glycerin or oil, and added in this way to the margarine. Coumarine is also said to be used, and Snelling has patented the addition of banana fruit or banana essence.

Vegetable Butter.—During the last few years a number of products have appeared on the market under the names of "Vegetable Butter" or "Nut Butter." These consist chiefly of carefully refined and deodorised coconut oil and palm-kernel oil, materials which have more recently been supplemented by the addition of margosa oil, shea butter, and mowrah-seed oil. Any suitable mixture of these or similar fats may be churned with milk, coloured, and salted, and finished off like genuine butter.

CHAPTER VIII

SALAD OILS

Salad Oils—Oils used for Culinary and Confectionery Purposes—Chocolate Fats.

Olive Oil.—No oil is so extensively used in the preparation of salad dressings as olive oil, and the more closely its characteristics can be imitated by other salad oils the greater is the demand for the latter.

There are several species of the olive tree, some of which are successfully cultivated in hot climates, but the oil used in Europe is mainly derived from different varieties of *Olea Europæa*. The fruit produced by these varies considerably in size and in colour, but the oils which they yield show a close similarity in chemical and physical characteristics, though they differ from one another in flavour and in colour.

Apart from the influence of soil and climate and of the variety of the olive tree, the flavour of the oil also depends upon the stage of growth at which the fruit is gathered, and upon the method of separating the oil from the pulp.

Fruit which is picked before it is quite ripe yields an oil with a somewhat bitter flavour, and therefore in preparing the finest grade of oil the olives are specially selected and pressed by hand between cloths. The resulting oil is washed with water to remove impurities, then decanted from the aqueous layer, and sold under the name of *virgin oil*.

The bulk of fine commercial olive oil, however, is separated by expression, the ripe olives being superficially crushed between mill-stones, and then expressed at a low pressure. The residue left in the press is broken up, mixed with hot water, and the liquid, consisting of the mixed oil and water, expelled by stronger pressure, and allowed to stand for the oil to separate. The flavour and colour of this oil is inferior to that of the cold-drawn product.

Subsequent grinding of this second residue, followed by another expression with hot water, yields an additional quantity of oil, whilst the amount still present is often extracted by means of carbon bisulphide or other volatile solvent. The oils finally obtained are generally utilised as lubricants, or in the manufacture of soap.

In most districts care is taken not to crush the olive stones until after the finest oil has been expressed, although according to Klein (*Zeit. angew. Chem.*, 1898, 847) there is no disadvantage in expressing the mixed kernel and fruit oil, provided the fruit is freshly picked. The general opinion of the trade, however, is that the flavour of the pulp oil is superior to that derived from the mixed pulp and kernels.

Oils which have been extracted by means of carbon bisulphide are known as "sulphocarbon" oils, whilst those which have been separated by means of petroleum spirit are termed "pyrene" oils.

The oils derived from olives which have been left for some time before expression are of an inferior kind, and are termed *huiles d'enfer*, *huiles tournantes*, etc. They contain a large amount of free fatty acids, and have a sharp, unpleasant flavour, which renders them unsuitable for food.

The finest qualities of oil are derived from the districts round Lucca and Leghorn, and from Provence. Large quantities of excellent oil are also exported from Spain, Portugal, Algiers, and Tunis, whilst California has now become an important oil-producing country.

The flavour is the chief criterion of the quality of olive oil, and a trained palate is able to detect slight differences which could not be recognised by any chemical tests.

The so-called *virgin oil* is pale yellowish-green in colour, and has but little odour, whereas the lower grades of oil obtained from the *marc* left in the press, as described above, vary in colour from greenish-yellow to light brown, and have a perceptible odour and a somewhat bitter flavour.

Even the purest olive oil will yield a deposit of " stearine " when exposed to a low temperature, but the amount varies with the kind of olive which yielded the oil. Thus it is particularly abundant in the case of Tunisian and Algerian oils, and it is therefore usual to remove a portion of this solid fat before putting the oil upon the market, under the name of " demargarinated " oil. The amount of " stearine " thus removed depends upon the temperature to which the oil is chilled before being pressed in a filter-press. Oils thus treated are sometimes described as " winter oils " (see Chapter III).

Olive oil consists chiefly of olein, with smaller quantities of the glycerides of linolic acid and of various solid fatty acids (mainly palmitic acid) which form the insoluble deposit—the so-called " stearine."

It belongs to the class of non-drying oils, and hence does not form a skin on its surface when exposed to the air, and when spread in a thin film upon glass takes many days to dry up. In this respect it differs from the semi-drying oils—cotton-seed, sesamé, and maize oils—which are frequently sold as salad oils, sometimes under descriptions that suggest they are olive oil.

The chief analytical characteristics of a typical olive oil are as follows:—

Sp. gr.	Saponification Value.	Iodine Value.	Hehner Value.	Melting-point of Fatty Acids.
0·918	191	82	95	24° C.

Olive oil is very frequently adulterated, the principal substances used for the purpose being cotton-seed, sesamé, maize, tea-seed, and lard oils. The vegetable oils may be detected by their general analytical values, and the two first by the characteristic colour reactions (see Chapter IX, pp. 139 and 141), whilst lard oil may be detected by the cholesterol test (p. 131).

During the war, the scarcity of olive oil, as, indeed, of all vegetable oils, led to the sale of large quantities of deodorised paraffin oil, coloured with an aniline dye, sometimes under the name of olive oil, but more frequently as "salad oil." Such adulteration may be readily detected by determining the saponification value, paraffin hydrocarbons being unsaponifiable. At the present time the principal adulterant of olive oil is *tea-seed oil*, which is very similar in its physical and chemical characters. The only method of detecting it yet discovered is by means of a colour reaction with nitric acid.

Maize Oil.—This oil, which is also known as *corn oil*, is obtained from the germs of the maize or Indian corn (*Zea mais*), and is used to a limited extent as an edible oil.

It resembles cotton-seed oil in its composition, and contains the glycerides of oleic, linolic, and palmitic acids, together with an appreciable quantity of those of volatile fatty acids, as is indicated by its relatively high Reichert-Meissl value (4 to 4·5).

Like cotton-seed oil, it belongs to the class of semi-drying oils, slowly forming a dry skin when exposed to the air in a thin film.

The following values are typical of a commercial oil :—

Sp. gr.	Saponification Value.	Iodine Value.	Hehner Value.	Melting-point of Fatty Acids.
0·9245	190	122	93·6	17° – 20° C.

The presence of cotton-seed oil, which is sometimes used to adulterate maize oil, would be shown by the characteristic colour reactions (p. 141). For the detection of maize oil in lard or in butter reliance would have to be placed upon the general analytical values and upon the results of the phytosteryl acetate test.

In the elaidin test maize oil yields a yellow butter-like mass after twenty-four hours.

Adulteration with mineral or resin oil may be detected by estimating the amount of unsaponifiable matter.

Arachis Oil.—The chief centre of the arachis oil industry is the South of France; and at Marseilles, in particular, enormous quantities of the nuts are expressed.

The oil obtained by the first expression in the cold is a pale yellow fluid which is extensively used as a salad oil. A large proportion of the oil obtained on subsequent expression is sold as a lower grade of salad oil, whilst the remainder, and also the oil obtained by hot pressure, is manufactured into soap. The total yield of oil is from 45 to 50 per cent.

As a rule, the salad oils (which are sometimes sold as "nut salad oil") have a distinct odour and flavour of the nut, but in the very finest grades, which also have but little colour, this flavour is hardly noticeable in the case of the freshly prepared product. Arachis oil becomes turbid at a much higher temperature and throws down a more abundant deposit of "stearin" than olive oil, and this has greatly interfered with its popularity as a salad oil in this country. The solidification point is usually about + 2° to + 3° C. Chemically it consists of the glycerides of hypogæic, oleic, linolic, palmitic, stearic, arachidic, and lignoceric acids. The most characteristic constituents are the two last fatty acids (amounting to about 5 per cent.). They are only slightly soluble in cold alcohol, and on this property are based several methods of separating them and of calculating from the result the proportion of arachis oil in, for example, an adulterated olive oil.

The physical and chemical constants of arachis oil vary considerably, as is shown in the following figures recorded by Sadtler and by Crossley and Le Sueur for oils of different origin :—

Oil.	Sp. gr. at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Free Acid (as Oleic Acid) per cent.	Melting-point of Fatty Acids, °C.
Virginian .	0·917	192·5	91·7	0·48	0·55	29
Spanish .	0·9175	190·7	94·2	1·60	0·79	34
African .	0·911	194·0	85·6	...	0·62	30
Indian. .	0·9223	190·1	98·5	Nil.	1·45	...

The highest figures recorded for the iodine value of arachis oil are 101–105 (Oliveri), whereas the lowest values fall well within the limits of those of olive oil.

Arachis oil is sometimes adulterated with cheaper oils, and notably with sesamé and cotton-seed oils. The determination of the analytical values and the characteristic colour reactions will probably afford information in such cases, while at the same time there would be a decrease in the amount of arachidic acid, or, rather, of the mixture of arachidic and lignoceric acids, which could be separated.

The methods of separating and determining this acid are described in Chapter IX, p. 142.

Sesamé Oil.—This oil also goes by the name of *teel oil* and *gingelly oil*, and in commerce is sometimes described as *French salad oil.*

It belongs to the same class of oils (*semi-drying*) as cotton-seed oil, which it also resembles in its chemical composition.

It contains the glycerides of oleic, linolic, palmitic, and stearic acids. The solid fatty acids amount to about 14 per cent. of the total fatty acids, whilst, according to Farnsteiner, the linolic acid is about 12 per cent.

The unsaponifiable matter contains phytosterol, a body termed *sesamin*, and a compound of the nature of a phenol, termed *sesamol.* It is to the presence of this substance that the characteristic furfural reaction (see Baudouin's test, p. 139) is due.

This active constituent may be removed from sesamé oil by treatment with animal charcoal, and the oil may also be rendered inert by prolonged heating over boiling water.

The oil can be bleached by treatment with animal charcoal and French chalk.

Sesamé oil has a pale yellow colour and a pleasant odour of the grain. It solidifies at a lower temperature (5° C.) than cotton-seed oil, and does not yield the large proportion of "stearine" given by the latter.

In the elaidin test it gives a reddish-brown partially solid mass of about the same consistence as the elaidin of cotton-seed oil.

Its iodine value (usually about 106) is somewhat lower than that of cotton-seed oil, except in the case of the oil from Russian seed, which has an iodine value of 114–115.

As is mentioned elsewhere, the addition of sesamé oil to margarine is compulsory in Germany, Austria, and Belgium, so that the product possesses a "latent colour" which may be developed by the use of the Baudouin reagent.

In addition to its use as a salad oil, and in pharmaceutical preparations, sesamé oil is employed as an adulterant of olive and almond oils; whilst, in turn, it is liable to be adulterated with arachis oil, cotton-seed oil, poppy oil, and rape oil.

The presence of the first may be detected by an estimation of the arachidic acid (p. 142), whilst Halphen's test will show the presence of cotton-seed oil.

The other oils are detected by the general physical and chemical characteristics, and, in the case of rape oil, by the characteristics of its principal fatty acid, erucic acid.

Cotton-seed Oil.—This oil, as has been already mentioned (p. 23), is expressed in enormous quantities in the United States, whilst there is a steadily increasing production in Egypt and India. In practice, a ton of cotton seed yields about 2½ cwt. of crude oil, which is then separated into "summer oil" and "foots" by refining (p. 40).

The bulk of the cotton-seed oil used for food in this country is derived from Egyptian seed, for the Indian oil is considered to have an unpleasant flavour.

Experiments made by Hooper, however, upon oils derived from American seed grown in India (*Ann. Report, Indian Museum*, 1910, 26), show that the fault lies with the method of screening the seed, and the process of refining the oil.

He finds that by treating Indian oils with the amount of alkali corresponding to the acidity and giving a subsequent thorough washing with water, the whole of the colouring matter, the so-called "bloom," and the acid taste are removed, and that the product has the light colour and bland flavour of refined Egyptian oil.

Thus, by removing all dirt from the seed and delivering the seed in sound condition, and washing the oil to a sufficient extent after the refining with alkali, there appears to be no reason why oils from Indian seed should be in any respect inferior to Egyptian oils.

Hooper's experiments also indicate that as much "stearine" could be separated from Indian oils as from American or Egyptian oils.

Cotton-seed oil consists chiefly of the glycerides of oleic and linolic acids, the latter, as is indicated by the iodine value, being present in much greater proportion than in olive oil, and amounting to about 17 or 18 per cent. of the total fatty acids. The glycerides of solid fatty acids which are present in solution, and separate out as "cotton-stearine" on chilling the oil, consist principally of those of palmitic acid with a small proportion of stearic acid (Hehner and Mitchell).

Owing to the presence of the large amount of linolic acid, cotton-seed oil belongs to the class of oils known as "semi-drying" oils, *i. e.* oils which thicken on exposure to the air, but, unlike the drying oils, do not form a dry film until after the lapse of a long time.

When exposed to a temperature of about 10° to 14° C., cotton-seed oil yields a deposit of the so-called "cotton-stearine" (*q. v.*), whilst the entire oil becomes solid at about the freezing-point of water. The stearin, which is separated by filtration (p. 38), is a useful by-product which is utilised in the preparation of margarine. The oil from which the "stearin" has been separated goes by the name of "winter" cotton-seed oil.

Oils which have been refined by treatment with alkali and separation of "stearin" have a mild taste and are practically devoid of free acids. They are widely employed both as salad oils and as substitutes for lard in cooking, but the bulk of the American oil is made up into margarine or used in the manufacture of soap.

Cotton-seed oil is a common adulterant of olive oil, and, owing to its forming a frequent ingredient of margarine, may find its way into butter.

In addition to the colour reactions, described on p. 141, it may be identified by the relatively high melting-point of its solid fatty acids (32° to 38° C.), and by its iodine value (106–115).

In the elaidin test (p. 138) it yields a butter-like mass of an orange colour, very different from the hard white elaidin produced by olive oil.

Cotton-seed oil contains about one per cent. of unsaponifiable matter consisting chiefly of phytosterol. The presence of cotton-seed oil in animal oils and fats may thus be confirmed by the phytosteryl acetate test (p. 131).

Sunflower Oil.—Enormous quantities of sunflower seeds are cultivated in Russia for the production of an edible oil, and most of the oil mills in that country are engaged in the industry.

The method of expression is similar to that used in this country for linseed. The seeds are first "screened" from dirt, particles of stalk, etc., and are then steamed and crushed to a paste, which is wrapped in hair-cloths and expressed in a hydraulic press. Expression by hand is still employed in some of the smaller mills.

When freshly obtained from clean seed, sunflower oil is a pale yellow fluid with a pleasant odour and flavour, but the second (hot) pressings are much darker in colour, and are used for illuminating purposes, and in the manufacture of varnish.

Sunflower oil has good drying properties, though these are less pronounced than in the case of poppy or linseed oil. It consists of the glycerides of oleic, linolic, and palmitic acids, and probably contains a small amount of linolenic acid.

Its iodine value (about 130) is considerably higher than that of cotton-seed oil.

When used as a salad oil it has the advantage of keeping fluid to a very low temperature, but its drying capacity, which causes a film to form rapidly upon the surface when exposed to the air, is a drawback from which olive and similar non-drying oils are free.

Sunflower oil is occasionally employed as an adulterant of olive oil. It would be detected by the increase in the iodine value, and, according to Jean, by its having a slight reducing action upon silver nitrate in Becchi's test (*q. v.*).

Poppy Oil.—The oil expressed from the seeds of the poppy (*Papaver somniferum*), which is cultivated in Egypt and Asia Minor, has a mild, bland taste, and is sometimes used as an edible oil.

Its chief use, however, is as a drying oil for paints, for which its good drying capacity and its light colour make it particularly suitable.

It consists of the glycerides of oleic, linolic, and linolenic acids, with a small proportion of those of solid fatty acids, including stearic and palmitic acids.

It shows considerable resemblance to sunflower oil in its chemical and physical characteristics, as is shown by the following typical values :—

Sp. gr.	Saponification Value.	Iodine Value.	Hehner Value.	Solidification Point.
0·926	194	136	95·4	– 15° to – 20° C.

If added in any considerable quantity to olive oil there would be an increase in the sp. gr. and iodine value of the latter.

Poppy oil is sometimes adulterated with sesamé oil, the presence of which may be detected by Baudouin's test.

Chocolate Fats

Cacao Butter.—In the manufacture of cocoa and chocolate a large proportion of the fat contained in the cocoa-bean is expressed, and forms a valuable by-product.

This fat, which is usually termed cacao butter, comes into the market in moulded slabs, weighing several pounds each.

It is a hard substance of a yellowish colour, having an aroma of cocoa, and, when broken, shows signs of crystalline structure.

Its flavour and high melting-point render it particularly suitable for the "cream" of chocolate creams, and large quantities of it are used for this purpose.

The chemical composition of cacao butter resembles that of other hard fats, the differences being due to a different proportion of the various glycerides.

It contains stearic, palmitic, lauric, and oleic acids, whilst arachidic, and a fatty acid termed theobromic acid, are also said to have been identified, though the presence of either is doubtful.

The hardness and high melting-point of the fat are due to the large proportion (about 40 per cent.) of stearic acid it contains.

The melting-point of the commercial product ranges from about 27° to 34° C.

The relatively low iodine value (usually between 32 and 36) indicates the presence of a much smaller amount of liquid fatty acids than of solid fatty acids, the former, according to Farnsteiner, consisting of oleic acid, and constituting 31 per cent. of the total fatty acids.

It has frequently been stated that cacao butter is not liable to become rancid. This, however, is not the case, for the fat, like other fats, does gradually decompose on exposure to light and air, though owing to its consistence and the low proportion of glycerides of liquid fatty acids present the process is not rapid, as in the case, for example, of coconut oil.

Cacao butter is frequently adulterated, the principal substances liable to be found being stearic acid, coconut oil, paraffin wax, beeswax, and various vegetable oils.

Cacao butter fetches too high a price to be used in the lowest grade of chocolate creams, and various substitutes are now sold.

Coconut and Palm-kernel Oil Stearines.—Among the most common of these cheaper products are the "stearines," obtained by expression from coconut oil and palm-kernel oil, both of which in their original condition are too soft, and melt at too low a temperature to be suitable for this purpose.

In preparing more solid fats these oils are melted and refined, then chilled down, and subjected to pressure in the cold in a hydraulic press. A fractionation is thus effected, the expressed portion, known as coconut or palm-nut olein, being much more fluid than the stearine left in the press, whilst the latter is more consistent than the original fat.

Thus, while the melting-point of coconut oil is usually about 23° C., that of the separate is about 30° C.

The following results were obtained by Sachs (*Chem. Rev. Fett Ind.*, 1908, xv. 30) in the examination of commercial samples of these stearines :—

	Melting-point, °C.	Sp. gr. at 100° C.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Melting-point of Fatty Acids. °C.
Hard coconut stearine .	29·3 to 29·5	0·8700	252	3·4	4·0 to 4·5	28·1
Palm-nut stearine	31·5 to 32	0·8700	242	2·2	8	28·5 to 29·5

Frequently these products are rendered still more consistent by the addition of a small proportion of an animal stearin or some vegetable fat of higher melting-point, such as Japan wax.

Thus a commercial preparation consisting of a mixture of coconut stearin with 25 per cent. of Japan-wax, melted at 34° to 35·5° C., or approximately at the same temperature as a good specimen of cacao butter.

The process of hardening oils by hydrogenation has also been extended to the treatment of semi-solid fats, such as coconut oil, and products of much higher melting point are thus obtained, while there is also a simultaneous deodorisation of the fat.

The following results published by Bömer and Leschly-Hansen (*Chem. Rev. Fett Ind.*, 1912, xix. 218, 247) show the effect of hydrogenation upon a typical coconut oil :—

	Melting-point, °C.	Solidification-point, °C.	Acid Value.	Saponification Value.	Iodine Value.
Coconut oil . . .	25·6	20·4	0·3	255·6	11·8
Coconut oil, hydrogenated	44·5	27·7	0·4	254·1	1·0

Other Vegetable Fats.—Of late years various exotic vegetable fats have been put upon the market as chocolate fats either in their pure state or in admixture with coconut or palm-nut stearins. These fats include dika fat, tankawang fat (Borneo tallow) and illipé fat.

Dika fat, which is obtained from the seed kernels of *Mangifera gabonensis* and other members of the same family, growing on the West Coast of Africa, is a hard fat, melting at about 39° C. (or higher than cacao butter), and having an iodine value (5) about the same as that of coconut oil.

Borneo tallow (*tankawang fat*) is derived from the seed kernels of *Shorea aptera* and other members of the *Dipterocarpi*. The native method of separating the fat is to suspend the kernels in baskets above boiling water, and when soft, to express them in primitive presses. According to Sachs (*loc. cit.*), Borneo tallow melts at 37·5° C., and has an iodine value of 30–31.

Illipé butter (*mahua butter*), which is derived from the seeds of *Bassia latifolia*, is a yellow fat, large quantities of which are eaten in India.

Nine samples of the Indian product examined by

Crossley and Le Sueur had melting-points ranging from 23° to 29° C., and iodine values of 58·4 to 67·8. The relatively low melting-point appears to depend upon the large proportion of glycerides of liquid fatty acids present, and this fat would probably yield a hard stearine on expression, or could be hardened by hydrogenation.

Others fats which might be used for this purpose, if they could be obtained in sufficient quantity, are shea butter, from the seeds of *Bassia Parkii* (melting at about 25° C.); Mafura tallow, melting at 35° to 42° C.; Mkani fat, melting at about 40° C.; Malabar or Piney tallow, produced by the East Indian tree, *Vateria indica* (melting at about 37° C.); and the products of various Brazilian oil seeds (p. 30).

Sachs (*loc. cit.*) states that favourite substitutes for cacao butter consist of a mixture of two-thirds of palm-nut stearine with one-third of coconut stearine, and of a mixture of 40 per cent. of Borneo tallow with 60 per cent. of coconut stearine.

CHAPTER IX

ANALYSIS OF RAW MATERIALS AND FINISHED PRODUCTS

General Methods of Analysis of Fats and Oils—Special Tests for Individual Oils — Analysis of Butter, Margarine, Lard, Cheese, Chocolate

The adulteration of fats and oils becomes year by year more scientific, the latest development of chemical research being prostituted to the purpose of enabling sophisticated articles to elude the vigilance of the public analyst, whose duty it is to detect such adulteration. A striking instance of this is furnished by the methods of adulterating butter described in Chapter V.

As was there mentioned, a method for the examination of pure butter, formulated by Reichert in 1879 and subsequently modified by Meissl and Wollny, was based on the presence of volatile fatty acids, such as butyric acid, in butter. Butter substitutes, as usually made, do not contain these volatile fatty acids, at any rate in appreciable quantity, except when coconut oil has been added, and this, therefore, afforded a means of detecting the presence of artificial in genuine butter. It has been found, however, that some manufacturers of butter substitutes, especially on the Continent, have actually added these volatile fatty acids, ostensibly to improve their flavour, but there can be little doubt with the real object of enabling the artificial product to be sold as genuine butter.

It is unfortunately the case that the unscrupulous manufacturer is generally slightly in advance of the examining authority, and as fast as the latter detects one form of adulteration, and devises means for its ready determination, some new form of fraud is invented to take its place.

As a result of this competition between expert adulterator and public analyst, the methods for the examination of edible fats are constantly being improved and increased, and some extremely elaborate tests have been suggested. In the following pages, however, only those most usually adopted in a works or commercial laboratory are described.

General Methods of Examination of Fats and Oils

Raw Materials.—The appearance, colour, and odour of the sample should be observed, and any characteristic feature recorded. The taste is also frequently of value in judging the purity of a fat or oil, but deductions from this can only be made after considerable experience.

The following physical and chemical data may be determined :—

Specific Gravity.—In the case of oils liquid at ordinary temperatures, this is usually taken at 15° C., the weight of a given volume of the oil being compared with that of the same volume of water, at 15° C., the symbol used to denote this being $d\frac{15^\circ}{15^\circ}$. If a sufficient quantity of the oil is available a Westphal balance or a hydrometer may be employed for the purpose ; if only a small quantity can be obtained, a specific gravity bottle or Sprengel or Nicol pycnometer should be used. This latter method is to be preferred where great accuracy is desirable. The specific gravity bottle or pycnometer must be first calibrated by filling it up to the mark with distilled water at 15° C., and weighing it.

The specific gravity of solid fats is taken at some higher temperature at which they are fluid, preferably at the temperature of a boiling water-bath, which will generally be found to be about 99° C. This is compared with the weight of a similar volume of water at 15° C., and is represented by $d\frac{99^\circ}{15^\circ}$.

The specific gravity of oils and fats is liable to increase with age, and also varies with the method of treatment during refining.

The specific gravity of butter fat is best taken at a temperature of 35° C., for reasons which are dealt with under the heading of "Butter," in Chapter V.

Free Fatty Acids.—These are determined by warming on the water-bath for a few minutes a weighed quantity (2 to 10 grms. according to the degree of acidity of the fat) of the fat or oil, with 25 c.c. of purified methylated alcohol, which has been neutralised immediately prior to use, with $\frac{N}{10}$ potassium hydroxide solution, and after adding phenol-phthalein solution, slowly running in from a burette $\frac{N}{2}$ or $\frac{N}{10}$ alcoholic potassium hydroxide solution until a faint permanent pink colour is produced. Each c.c. of $\frac{N}{2}$ or $\frac{N}{10}$ alkali corresponds to 0·141 or 0·0282 grm. respectively of free fatty acids, expressed as oleic acid, and from this the percentage of acidity is calculated.

The free acidity is frequently expressed as the *acid* *value,* which represents the number of milligrams of potassium hydroxide, KOH, required to neutralise the acidity in 1 grm. of oil or fat.

Example.—If 6·656 grms. fat required 1·5 c.c. $\frac{N}{10}$ alcoholic potassium hydroxide solution to neutralise it, then $\frac{1·5 \times 0·0282 \times 100}{6·656} = 0·63$ per cent. free fatty acids, expressed as oleic acid.

The *acid value* in this case would be

$$\frac{1·5 \times 0·00561 \times 1000}{6·656} = 1·26.$$

The maximum permissible limit for free acidity depends on the nature of the fat or oil. For edible tallows it should not exceed 3 per cent., for lard 0·5 per cent., and for coconut oil 2 per cent.

Saponification Value.—It has been shown in Chapter I how the various glycerides contained in fats and oils are split up or saponified by the action of caustic alkalies, one molecule of a triglyceride such as stearin requiring three molecules of potassium hydroxide for its saponification (cf. p. 5).

The composition of the various fats and oils being fairly constant, the amount of alkali required for the saponification of any given weight is also nearly constant. Koettstorfer first utilised this fact in 1879 for the analysis of butter fat, and it has now become the basis of one of the most important factors in the analysis of nearly all fats and oils, the amount of any fat which is saponified by 1 grm.-molecule or 56·1 grms. of potassium hydroxide being termed its *saponification equivalent.*

The more usual method of expressing the same thing is the number of milligrams of potassium hydroxide required to saponify 1 grm. of fat, which is called the *saponification value.* The difference between the saponification and acid values is spoken of as the *ester value.*

To convert saponification equivalent into saponification value, it is merely necessary to divide 56·1 by the saponification equivalent, and multiply the quotient by 100.

To determine the saponification value, about 2 grms. of the fat or oil are weighed out into a conical flask of about 200 c.c. capacity, 25 c.c. of *neutral* purified methylated spirit added, and 25 c.c. of an approximately $\frac{N}{2}$ alcoholic solution of potassium hydroxide run in from a burette, similar quantities of purified methylated spirit and alcoholic potassium hydroxide solution being also placed in another flask to serve as a blank test. The two flasks are now fitted with reflux condensers (which may be simply glass tubes, about four feet long and half an inch in diameter, inserted through a cork), and are placed on a steam or water bath. The contents are then boiled until saponification of the fat is complete, which may take from thirty to sixty minutes, and is known to be accomplished when all globules of oil disappear. A few drops of phenol-phthalein solution are now added to each flask, and $\frac{N}{2}$ hydrochloric or sulphuric acid carefully run in from a burette until the pink colour is discharged. The difference in the amount of acid required by the contents of the two flasks indicates the quantity of potassium hydroxide required to saponify the weight of fat or oil taken.

Example.—2·1314 grms. fat required 10·7 c.c. $\frac{N}{2}$ hydrochloric acid to neutralise unabsorbed alkali.

In the blank test 25 c.c. of approximately $\frac{N}{2}$ alcoholic potassium hydroxide solution required 25·6 c.c. of $\frac{N}{2}$ hydrochloric acid to neutralise it.

25·6 — 10·7 = 14·9 c.c. $\frac{N}{2}$ alcoholic potassium hydroxide solution required to saponify the fat, and—

$\frac{2{\cdot}1314 \times 1000 \times 2}{14{\cdot}9} = 286{\cdot}1$ saponification equivalent,

and $\frac{56{\cdot}1 \times 100}{286{\cdot}1} = 196{\cdot}1$, the saponification value.

If the quantity of fat or oil employed for the estimation of acidity is only about 2 grms., the saponification value may also be determined on the same quantity. After proceeding as described above for the acidity estimation, 25 c.c. of approximately $\frac{N}{2}$ alcoholic potassium hydroxide solution are added to this, and the process continued as described above.

Iodine Absorption.—This test, devised by Hübl in 1884, and subsequently modified by Wijs, by Hanus, and by Waller, is based upon the capacity of unsaturated fatty compounds to absorb iodine and other halogens, with formation of addition compounds. The amount of iodine or of equivalent halogen absorbed is therefore a measure of the unsaturated compounds present in a fat, and is very fairly constant within certain limits for any given fat in the fresh condition. The action of Hübl's solution is attributed by Ephraim to the presence of iodine monochloride, but by Wijs to that of hypo-iodous acid. The percentage of iodine absorbed is usually recorded as the *iodine number* or *iodine value.*

In Hübl's method, two solutions are required—(1) containing 25 grms. iodine in 500 c.c. of absolute alcohol, and (2) containing 30 grms. mercuric chloride in 500 c.c. of absolute alcohol. These solutions should be kept separate, and only mixed about twelve to twenty-four hours before use.

The process is carried out as follows:—Into a tightly fitting stoppered bottle is introduced 0·2 to 0·6 grm. of the fat, 10 c.c. chloroform added, and 25 c.c. of the mixed Hübl solution run in from a burette. The bottle is then firmly stoppered, and allowed to stand in a dark place for four hours, a similar bottle containing the same quantities of chloroform and Hübl solution being placed by its side as a blank experiment.

At the end of the four hours, 20 c.c. of a freshly prepared 10 per cent. potassium iodide solution and 150 c.c. of water are added to each bottle, and the excess of iodine titrated with recently standardised $\frac{N}{10}$ sodium thiosulphate solution, the bottles being vigorously shaken during the titration, and fresh starch solution used for determining the final point. The difference in the number of c.c. of $\frac{N}{10}$ sodium thiosulphate solution required by the contents of the two bottles is a measure of the iodine absorbed by the fat. This figure, multiplied by the iodine equivalent of the sodium thiosulphate solution (found by titrating it with a known weight of pure resublimed iodine), and by 100, and divided by the weight of fat taken, gives the iodine value of the fat.

Example.—0·539 grm. oil taken. Blank bottle, with iodine solution and chloroform only, required 61·4 c.c. $\frac{N}{10}$

thiosulphate; bottle containing oil required 25 c.c. $\frac{N}{10}$ thiosulphate. The iodine equivalent of the $\frac{N}{10}$ thiosulphate solution was found to be 1 c.c. = 0·0126 grm. I.

Then $\frac{(61{\cdot}4 - 25{\cdot}0) \times {\cdot}0126 \times 100}{{\cdot}539} = 85{\cdot}1$ iodine value.

Wijs' Method.—The Hübl method has now to a very large extent been displaced by the Wijs process, in which the iodine is absorbed by the fat much more quickly, only about thirty minutes' contact being required. The Wijs iodine reagent consists of a solution of iodine monochloride in glacial acetic acid, and may be prepared either by weighing out 7·9 grms. of iodine trichloride (which must be done in a weighing bottle) and 8·7 grms. of iodine, dissolving these separately in glacial acetic acid, and mixing and making the solutions up to a litre with glacial acetic acid; or dissolving 13 grms. of iodine in a litre of glacial acetic acid, and passing chlorine into the solution until the iodine is all converted into the iodine monochloride—a point which may be determined by the gain in weight, or, with a little practice, by the change in colour of the solution. The details of the process are closely similar to those in the Hübl method, except that it is preferable to dissolve the fat in carbon tetrachloride instead of in chloroform.

Bromine Absorption.—This is similar in principle to the iodine absorption, and though numerous processes, both gravimetric and volumetric, have been proposed for its determination, it has now been almost entirely superseded by determination of the iodine absorption. A process devised by McIlhiney (*J. Amer. Chem. Soc.*, 1894, 295, and 1899, 1084), however, deserves attention, for it estimates both the added and the substituted bromine.

The weighed quantity, say 0·5 grm. of the oil or fat, is dissolved in 10 c.c. of chloroform, and 20 c.c. $\frac{N}{3}$ solution of bromine in chloroform added. After two or three minutes 20 to 30 c.c. of a 10 per cent. potassium iodide solution are added, and the liberated iodine titrated with standard $\frac{N}{10}$ thiosulphate, the result giving the bromine forming addition compounds. After this, 5 c.c. of neutral 2 per cent. potassium iodate solution are introduced, and the liberated iodine titrated, the result in this case corresponding to the hydrobromic acid formed by the bromine in producing substituted bodies, or, in other words, giving the *bromine substitution value*.

Titre, or Sodidifying Point of the Fatty Acids.—Many methods for determining the melting and solidifying points of fatty matters have been proposed, but modifications of the *titre test*, due to Dalican, are now most generally adopted. This test consists in determining the solidifying point of the fatty acids separated from a fat or oil, a figure which is an important characteristic of most fats, and in the case of tallows is largely employed as the basis for their commercial valuation. It is, of course, essential that in the preparation of artificial butters from a standard formula the firmness of the fats used should be as nearly as possible constant, and this is best determined by the titre test.

The test is carried out by first saponifying the fat with alcoholic sodium hydroxide solution, decomposing the resulting soap with dilute sulphuric acid, and after washing and drying the liberated fatty acids, determining their solidifying point. One ounce of the sample is melted in a shallow porcelain basin on a water-bath, and 30 c.c. of a 25 per cent. solution of sodium hydroxide added, together with 50 c.c. of redistilled methylated spirit. The contents of the basin are now evaporated on the water-bath, with constant stirring, until a pasty mass of soap is formed, and this is redissolved in a further 50 c.c. of redistilled methylated spirit, and again evaporated to dryness on the water-bath. The solid soap thus obtained is dissolved in water, sufficient dilute sulphuric acid added to decompose it, and the whole warmed until the fatty acids melt to a clear oily liquid on the surface. The water underneath is now siphoned off, more distilled water added to wash out any remaining trace of mineral acid, and again siphoned off, this treatment being repeated until the washings are no longer acid to litmus paper. The melted fatty acids are next poured on to a dry filter paper, which is placed in a funnel resting on a beaker, and the latter is placed either in the water-bath or in an air-oven at about 100° C. until the clear fatty acids have filtered through it.

From 10 to 15 grms. of these dry fatty acids are transferred to a wide test tube, about six inches long and one inch in diameter, which is inserted through a cork into a flask or wide-mouthed bottle, to protect the tube from draught. The tube is closed with a loosely fitting perforated cork, through which passes a short range thermometer (0° to 60°), accurately graduated in fifths of a degree centigrade, and having its bulb just immersed in the fatty acids as near the centre as possible.

The temperature is now raised to a few degrees above the melting-point of the fatty acids, and allowed to cool down without stirring. As soon as the fatty acids just begin slowly to solidify, they are stirred round gently with the thermometer, the temperature on which will gradually fall till a minimum point is reached. Stirring is now discontinued, and the rise in temperature, which is produced by the heat given out by the acids in crystallising, is observed. The maximum temperature attained by the fatty acids during this rise is the "titre" of the sample.

Refractive Index.—The determination of the refractive power of a fat or oil, or of its fatty acids, is frequently very useful in judging the purity of a sample, or in drawing conclusions as to the composition of a mixture of fats.

The refractive index itself may be either directly determined by means of an Abbé total reflection refractometer, or, as is more usual in the case of butter, the refractive power may be read off on an arbitrary scale by means of a Zeiss butyro-refractometer.

The oleo-refractometer of Amagat and Jean (*Analyst*, 1890, 97), is also a convenient instrument.

One of the great advantages of this test is the ease and rapidity with which a number of samples may be examined, whilst a further advantage of the Abbé and Zeiss instruments is that only a very small quantity of the sample—5 or 6 drops—is necessary.

The different forms of apparatus are fully illustrated and described in the catalogues of most firms supplying chemical apparatus, and it is therefore unnecessary to give a description here.

Different chemists use various temperatures for determining refractive indices, but that most usual for oils and fats, with the exception of butter, is 60° C. The best temperature of observation for butter is 40° C.

Unsaponifiable Matter.—The amount of unsaponifiable matter present in the ordinary animal and vegetable fats is very small, and the addition of any paraffin or other hydrocarbon is therefore readily detected by estimating the unsaponifiable matter. The usual method is to saponify about 5 grms. of the fat, dissolve the soap in water, and extract the unsaponified fatty matter with ether. The saponification is effected by boiling the fat with 50 c.c. of approximately $\frac{N}{2}$ alcoholic potassium hydroxide solution under a reflux condenser, with frequent agitation, for about an hour. The soapy solution is then evaporated to dryness in a porcelain basin on a steam or water bath, and the soap obtained is dissolved in about 200 c.c. of hot water and transferred, as soon as sufficiently cool, to a 10 oz. separating funnel. To this is now added 50 c.c. of ether, and the whole well shaken, and allowed to separate. The aqueous soap solution at the bottom is now run into another similar separator, and the ethereal extract washed with water to remove any soap dissolved therein. The washings are added to the aqueous soap solution, which is again extracted with a second 50 c.c. of ether, separated, the ethereal extract washed with water, and the extraction repeated a third time. The three washed ethereal extracts are then transferred to a weighed flask, the ether distilled off on a water-bath, and the residue dried in the oven at 100° C. till constant in weight. This residue is the unsaponifiable matter in the weight of fat taken, whence the percentage may be calculated.

Difficulty often occurs during this process through the formation of an emulsion between the ethereal and the aqueous solutions, which prevents a sharp separation of the two layers. To overcome this, various expedients are recommended, such as the addition of a few c.c. of alcohol or glycerin or of more ether or water, careful warming, or gentle rotation.

The unsaponifiable matter may consist of cholesterol, a constituent of many animal fats, of phytosterol, a substance similar to cholesterol found in vegetable fats, of solid alcohols, such as cetyl and ceryl alcohols, present in spermaceti and Chinese wax, or of hydrocarbons, which do not occur naturally in common animal or vegetable fats, although they are present in shark-liver oils, and are occasionally added as adulterants to other oils (see p. 106).

To examine the unsaponifiable matter for cholesterol and phytosterol a small quantity is dissolved in acetic anhydride, and one drop of the solution added to one drop of 50 per cent. sulphuric acid on a white porcelain tile, when, if either is present, a blood-red to violet coloration is produced. They may be distinguished from each other by their crystalline form, cholesterol crystallising in laminæ, phytosterol in needle-shaped tufts; or by the melting points of their acetates, cholesteryl acetate melting at 114·3° to 114·8°, and phytosteryl acetate at 125·6° to 137° C.

The fact that the unsaponifiable matter of animal fats contains cholesterol, whilst that of vegetable oils and fats contains phytosterol, has been made the basis of a test for detecting the presence of vegetable oils and fats in butter or lard. This test, which was first proposed by Bömer (*Zeit. Untersuch. Nahr. Genussm.*, 1898, 81), consists in saponifying the fat with alcoholic potassium hydroxide, and extracting the unsaponifiable matter with ether, which is then distilled off, and the residue recrystallised from alcohol. The process has been subsequently improved by converting the cholesterol or phytosterol into the acetic esters by heating it with acetic anhydride, and determining the melting point of the resulting ester. As mentioned above, that of cholesterol melts at about 114° C., that of phytosterol at 125·6° to 137° C., and, according to Bömer, an acetate melting at 117° to 118° C. corresponds to an addition of 1 to 2 per cent. of vegetable oil; at 120° to 121° C., to an addition of 2 to 3 per cent. of vegetable oil; and at 123° to 125° C., to an addition of 3 to 4 per cent. of vegetable oil.

The following method of carrying out this test, which is known as the *phytosteryl acetate test*, is described by Revis and Bolton (Allen's *Commercial Organic Analysis*, ii. p. 301).

Fifty grms. of the clear fat are boiled with 75 c.c. of 95 per cent. alcohol, cooled, and the alcohol poured off, a second extraction being made with a further 75 c.c. of alcohol. These combined extracts, which will contain the greater part of the cholesterol and phytosterol and some fat, are transferred to a porcelain basin, and an excess of solid sodium hydroxide added, the mixture being then evaporated, with gentle stirring. After most of the alcohol has evaporated, more than sufficient sodium bicarbonate is added to convert the excess of sodium hydroxide into sodium carbonate, then some sand, and the whole evaporated to dryness, ground up in the dish, and extracted with light petroleum spirit. The residue from the ether is heated with 5 c.c. of (approximately) $\frac{N}{2}$ alcoholic sodium hydroxide solution and again evaporated to dryness, with sand. A fresh extraction with petroleum spirit is made, followed by evaporation, and the residue is taken up with the smallest possible quantity of absolute alcohol. If necessary, the solution is boiled with animal charcoal and some 95 per cent. alcohol, filtered and evaporated to dryness. The crystals obtained are examined microscopically, then converted into their acetate by boiling them with acetic anhydride in a covered watch-glass, evaporating off the excess of acetic anhydride on the water-bath, and recrystallising them from absolute alcohol.

Further tests for cholesterol have also been published by Lifschütz (*Ber. Deut. Chem. Ges.*, 1908, 252–5) and Golodetz (*Chem. Zeit.*, 1908, 160).

The method of the former depends on the oxidation of cholesterol to oxycholesterol ester and oxycholesterol. A few mgrms. of the unsaponifiable matter are dissolved in 2 to 3 c.c. of glacial acetic acid, a little benzoyl peroxide added, and the solution boiled, after which four drops of strong sulphuric acid are added. If cholesterol is present, a violet-blue or green colour is produced, the violet colour being due to oxycholesterol ester, the green to oxycholesterol.

Golodetz has devised two tests: (1) the addition to a small quantity of the unsaponifiable matter of one or two drops of a mixture of 5 parts of concentrated sulphuric acid with 3 parts of formaldehyde solution, this reagent turning cholesterol a blackish-brown colour; and (2) the addition of one drop of 30 per cent. formaldehyde solution to a solution of the unsaponifiable matter in trichloracetic acid, when, if cholesterol is present, an intense blue coloration is produced.

Another method of separating cholesterol and phytosterol has been based by Marcusson and Schilling (*Chem. Ziet.*, 1913, xxxvii., 1901) upon the fact that they combine with digitonin to form insoluble compounds.

Various modifications of this method have been devised, one of the most simple of which is that suggested by Fritzsche.

The melted fat (50 grms.) is continuously stirred for five minutes, at 60° to 70° C., with 20 c.c. of a 1 per cent. alcoholic solution of digitonin. In the case of oils and semi-solid fats the mass is filtered immediately, with the aid of suction, in a Buchner's funnel, and the residue washed with six successive portions of 5 c.c. of ether; if solid fats are under examination 20 c.c. of chloroform are added to the hot liquid, and the separated insoluble portion washed twice with chloroform (4 c.c. each time), and then with six portions of ether to remove all the fat.

The residue of digitonide or digitonides is dried for five minutes at 30° to 40° C., dissolved in 2 c.c. of hot acetic acid, and the solution boiled for five minutes in a test-tube provided with a vertical tube to act as a condenser, and then filtered through cotton wool.

The tube and filter are washed twice with 0·5 c.c. of hot absolute alcohol, and the united filtrate and washings evaporated on the water-bath in a current of air. The residue of phystosterol or cholesterol acetate is dissolved in 0·5 to 1 c.c. of absolute alcohol, and the crystals drained on a porous tile, and examined as described above.

Of the less frequently used methods of examination the following may be mentioned :—

Valenta's Acetic-acid Test, which depends on the solubility of most oils and fats in hot glacial acetic acid of 1·0562 sp. gr., the temperature at which a warmed mixture of 3 c.c. melted fat and 3 c.c. acetic acid becomes turbid on cooling being noted.

The test has been slightly modified by Pearmain and

Moor, who used a short stoppered tube, into which is weighed 2·75 grms. of the fat or oil, followed by 3 c.c. of acetic acid. The tube is then stoppered and heated in a water-bath, the temperature being raised until the contents of the tube become clear on shaking, after which the source of heat is removed, and the tube allowed to cool down gradually in the centre of the water-bath until the contents again become slightly turbid. The temperature at which this takes place is recorded, and is a fairly definite figure for any given oil. This test is of some value in the examination of butter for margarine, as is pointed out in Chapter V, p. 69; the temperature at which the solution of the latter in acetic acid becomes turbid being very much higher than that of the former.

The following are the figures obtained by Pearmain and Moor by the above method :—

	°C.
Butter fat	23–38
Margarine	94–97
Lard	97–99
Tallow	96–99
Cotton-seed oil	71–89
Sesamé oil	90–97
Olive oil	83–91

The drawback of this test is that slight variations in the strength of the acetic acid, such as inevitably result from opening the bottle, cause considerable variations in the temperatures of turbidity. To obviate this, it is advisable to compare the results with those given by specimens of butter fat of known purity.

A solvent which can be exposed to the air for several hours without materially affecting the turbidity temperature of an oil dissolved in it is a mixture of equal parts of 90 to 92 per cent. alcohol and amyl-alcohol. This modification of the test has been devised by Fryer and

Weston (*Analyst*, 1918, xliii. 3), who recommend that pure almond oil should be used to standardise the solvent, which should be diluted so as to give a turbidity temperature of about 70° C. with that oil. Another advantage of this solvent is that the results are not materially affected if the oil has been heated prior to the test.

To obviate the drawback of the solidification of the acetic acid in cold weather Parkes (*Analyst*, 1918, xliii. 82), dilutes the solvent with water and a lower fatty acid such as butyric acid.

Maumené's Test, first proposed in 1852, consists in observing the rise of temperature which takes place when the fat or oil is mixed with concentrated sulphuric acid. Various methods of applying the test have been proposed by different authorities, that suggested by Archbutt (Allen's *Commercial Organic Analysis*) being as follows: Fifty grams of oil are weighed into a 200 c.c. beaker, and the latter immersed in a capacious vessel of water, together with the bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20° C. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard drum, or a wider beaker. The immersed thermometer is then observed, and the temperature recorded. Ten c.c. of the concentrated sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about one minute, the mixture must be constantly stirred with the thermometer, and the agitation continued till no further rise of temperature ensues. This point is readily observed, as the mercury remains constant for a minute or two, and then begins to fall. Very different results are obtained according to the strength of acid employed, the best strength being 97 per cent.

Thomson and Ballantyne (*Journ. Soc. Chem. Ind.*, 1891, x. 233) proposed to determine the "*specific temperature reaction*" of the oil, this being obtained by noting (1) the rise of temperature produced when 50 grms. of water are mixed with 10 c.c. of strong sulphuric acid in the same vessel and under the same conditions as those to be used for mixing the acid and oil; (2) mixing the oil and acid as described above, and then multiplying the rise in temperature produced by the oil-acid mixture by 100, and dividing by the rise in temperature given by the water-acid mixture. The following figures are given by Thomson and Ballantyne:—

Oil.	Temperature. Water = 100° C.
Olive	89–95°
Arachis	105–137°
Cotton-seed	163–170°

It has been shown by one of the authors (M.; *Analyst*, 1901, xxvi. 169), that if the oil be dissolved in an inert solvent, such as carbon tetrachloride, the rise in temperature on adding sulphuric acid is usually proportional to the iodine value, *i.e.* the degree of unsaturation of the oil.

Hence, since, in most cases, the Maumené test conveys little more information than can be obtained by the bromine thermal test or Wijs's rapid method of determining the iodine value, it is not often used at the present time; but inasmuch as it is still referred to in textbooks, and is quoted in recorded analyses of oils, it is not yet obsolete.

Bromine Thermal Value.—The heat reaction with bromine was utilised by Hehner and Mitchell (*Analyst*, 1895, xx. 146) as a rapid means of ascertaining the degree of unsaturation of oils and fats, a weighed quantity of the sample being dissolved in chloroform or acetic acid, and the rise in temperature on addition of bromine noted. The oil, chloroform, and bromine having first been brought to the same temperature, 1 grm. of oil is dissolved in 10 c.c. of chloroform in a Dewar's vacuum-jacketed test tube, and 1 c.c. of bromine added from a special pipette. This consists of a 1 c.c. pipette with a narrow tube, bent twice at right angles, attached to its top, the horizontal portion of the tube containing caustic lime kept in position by asbestos plugs. The mixture is immediately stirred, and the rise in temperature measured with a thermometer graduated in fifths of a degree. In the case of most ordinary oils and fats a relationship is shown to exist between the rise in temperature and the iodine value, so that this ratio having once been ascertained for the apparatus employed, the iodine value may be readily calculated from the rise in temperature observed on adding the bromine.

A modification of the method has been devised by Marden (*J. Ind. Eng. Chem.*, 1916, viii. 121) in which the heat of bromination is calculated into calories per gram of oil. He finds that any pronounced difference between the calculated iodine value and that actually determined, must be attributed to there being a greater degree of substitution by the bromine than the iodine.

Elaidin Test.—The best method of applying the test is to make use of the action of nitric acid on mercury, a reagent being prepared by dissolving 1 c.c. of mercury in 12 c.c. of cold nitric acid of 1·42 sp. gr. When this is shaken with the oil in a wide-mouthed stoppered bottle in the proportion of 2 c.c. of reagent to 50 c.c. of oil, the shaking being repeated at intervals of ten minutes for two hours, and the temperature kept constant at not less than 25° C., a bright lemon-yellow coloured solid mass is obtained with olive oil. The products of the reaction with almond, lard, sperm, and archis oils are also solid, but those yielded by rape, sesamé, cotton-seed, sunflower, cod-liver, and porpoise oils have a consistence resembling that of butter, whilst those from linseed and other drying oils are liquid.

The preceding methods of examination are more or less generally applicable to all edible fats and oils, but there are numerous special tests applicable only to individual oils, of which the following are the most important. The application of these is also discussed more generally in the sections dealing with the special oils.

SESAMÉ OIL

Baudouin's Test.—This is carried out by dissolving 0·1 grm. of cane sugar in 10 c.c. hydrochloric acid of sp. gr. 1·2 and adding this to 20 c.c. of the oil under examination, shaking the mixture thoroughly and allowing it to stand. The presence of as little as 2 per cent. of sesamé oil imparts a product obtained by treatment of the oil with nitrous acid and the time required for its solidification being observed.

A modification of this, consisting in adding 0·1 c.c. of a 2 per cent. alcoholic solution of furfural to the hydrochloric acid instead of the 0·1 grm. sugar, was devised by Villavecchia and Fabris, who found the reaction to depend upon the formation of furfural; whilst Wauters suggested that instead of mixing the reagent with the oil, the latter should be poured upon the reagent, under which conditions less than 1 per cent. will impart a crimson colour to the surface of contact.

Sprinkmeyer and Wagner (*Zeit. Nahr. Genussm.*, 1905, x. 347–353) have still further increased the delicacy of the test, so that as little as 0·1 per cent. of sesamé oil may be detected. In their process about 100 grms. of the filtered fat are twice extracted with 20 to 30 c.c. of glacial acetic acid at 60° C. The acid extracts are separated and evaporated, and the residue tested as described above. In the case of butter containing colouring matter, which may interfere with the reaction, the latter may be removed by evaporating the acetic acid residue with 10 c.c. of alcohol and 5 c.c. of saturated barium hydroxide solution, and extracting the residue several times with light petroleum spirit, which is then evaporated, and the final residue treated with the furfural solution.

Tocher's Test.—A freshly made solution of 1 grm. of pyrogallol in 15 c.c. of concentrated hydrochloric acid is shaken in a separating funnel with 15 c.c. of the oil, and allowed to separate. The aqueous liquid is then drawn off, filtered, and boiled for about five minutes, when, if sesamé oil is present, it appears red by transmitted and blue by reflected light.

Bishop's Reaction.—On exposing sesamé oil to the air for several days in the presence of light, and then shaking it with one and a half times its volume of hydrochloric acid (sp. gr. 1·19) the acid layer assumes a green coloration, the intensity of which depends upon the age of the oil.

Kreis (*Chem. Zeit.*, 1899, xxiii. 802) found that this green colour was caused by oxidation products of the glycerol, and suggested the use of the reaction as a test for rancidity in other fats. Thus he found that old butter, and old olive oil, which gave no coloration by themselves with hydrochloric acid, gave the green coloration when mixed with fresh sesamé oil.

TEA-SEED OIL

The oil expressed in China from the seeds of the tea-plant closely resembles olive oil in its analytical characteristics, its iodine value ranging from about 84 to 90. It is therefore now extensively used for the adulteration of olive oil, and cannot be detected by the ordinary methods of analysis.

The only reaction yet devised for its detection is that of Cofman and Nicoresti (*Pharm. J.*, 1920, civ. 139). The suspected oil is shaken with a mixture of sulphuric and nitric acids and water, and the tube then immersed for twenty minutes in boiling water. In the presence of tea-seed oil in a proportion of not less than about 20 per cent. the oil layer will become pink.

COTTON-SEED OIL

There are two well-known tests for this oil, those of Becchi and Halphen, both of which have undergone various modifications.

Becchi's, or the silver-nitrate test, requires the preparation of two solutions : (1) containing 1 grm. of silver nitrate dissolved in 200 c.c. of alcohol (98 per cent. by volume), to which is added 40 c.c. of ether and 0·1 grm. of nitric acid; and (2) a mixture of 15 c.c. of rape oil with 100 c.c. of amyl-alcohol. Ten c.c. of the oil to be tested are mixed in a test-tube with 1 c.c. of solution (1), and then shaken with 10 c.c. of solution (2). The mixture is now divided into two equal parts, and one half immersed in boiling water for fifteen minutes, after which it is withdrawn and compared with the unheated portion. In the presence of cotton-seed oil a reddish-brown coloration is developed.

Halphen's Test.—Equal parts of the oil or fat (or its fatty acids), amyl-alcohol, and a 1 per cent. solution of sulphur in carbon bisulphide, are heated together in a test-tube placed in a boiling-water bath until effervescence ceases, and then transferred to a boiling brine bath for about an hour, when, if cotton-seed oil is present, a pink coloration is produced. The reaction may be rendered much more rapid, according to Rupp (*Zeit. Untersuch. Nahr. Genussm.*, 1907, xiii. 74), by heating the mixture in a stoppered flask.

The production of a coloration with Becchi's or Halphen's reagent does not invariably prove the presence of cotton-seed oil, as the pure fat of animals fed with cotton-seed cake, even some long time previously, has been found to give a slight reaction. On the other hand, failure to obtain a reaction does not prove the absence of cotton-seed oil, since heating the oil to 250° C. causes it to give negative results in these tests.

Arachis Oil

The great similarity in the properties of this oil and olive oil renders some means of distinguishing one from the other necessary, and a process for the purpose has been based on the different chemical composition of the fatty acids, the arachis oil containing a considerable proportion of arachidic and lignoceric acids.

This arachidic acid (the term also being used to include the lignoceric acid) may be determined by the following process due to Renard and modified by Lewkowitsch: About 10 grms. of the oil are saponified with alkali, as described under the "titre test," the soap dissolved in water, excess of alkali neutralised with acetic acid, and the lead salts of the fatty acids precipitated by addition of a solution of lead acetate, filtered off, and extracted with ether, all but the palmitate and arachidate being dissolved. These latter are decomposed with hydrochloric acid, the fatty acids separated from lead chloride, and dissolved in 50 c.c. of hot 90 per cent. alcohol.

On cooling this solution, arachidic acid will crystallise out if arachis oil is present, and the amount of arachidic acid may be estimated, if desired, by filtering it off, and washing it twice with 10 c.c. of 90 per cent. alcohol, and once with alcohol of 0·890 sp. gr. The residue on the filter is now extracted with boiling absolute alcohol, in which arachidic acid is soluble, the solution evaporated to dryness, and the arachidic acid weighed.

This amount has to be corrected by the addition of 0·0025 grm. for each 10 c.c. of 90 per cent. alcohol used in the crystallisation and washing if the treatment has been carried out at 15° C., or 0·0045 for 10 c.c. if it was done at 20° C. Arachis oil contains about 5 per cent. of arachidic acid, so that twenty times the total amount of arachidic acid represents the quantity of arachis oil in the sample under examination. The melting point of arachidic acid is 71°–72° C.

Butter

An analysis of butter for the purpose of the Food and Drugs Act should comprise determination of the water and examination of the fatty matter, together with tests for colouring matter and preservatives. In addition, estimations of the casein, ash, and salt are also sometimes made.

The effect of heating a little of the sample in a spoon is a useful rough indication of its purity. Pure butter produces considerable foam, and turns brown, but, as a rule, butter substitutes do not foam appreciably, and unless specially prepared to do so (see Chapter V, pp. 67 and 102), do not become brown.

Water.—The determination of water may be made by weighing out about 5 grms. of the butter in a platinum dish and placing it in a hot-air oven at a temperature of 100°–105° C., the drying being continued until the weight is constant.

Examination of the Fat.—A quantity of the butter fat is prepared by heating about 50 grms. of the sample on the top of a water-bath until it has completely melted, and the water and casein have separated to the bottom, when the clear fat is decanted off and filtered through a dry, warm filter paper. The filtered fat should be clear and bright, and is then ready for examination.

Many of the general methods already described for the examination of oils and fats are applicable, and furnish useful information as to the purity of butter. Such, for example, are the specific gravity, the saponification value, the refractive power, and Valenta's acetic-acid test, the variations in which are discussed on p. 134.

Refractive Power.—The instrument most usually employed is the Zeiss butyro-refractometer, which consists of an Abbé double prism, which opens for the reception of a few drops of the melted and, preferably, filtered fat. A telescope is attached for reading the refraction on an arbitrary scale graduated from 5°–105°. The prism should be maintained at 40° C. while the observation is being made. At this temperature the reading for pure butter is usually about 35°–38°. If the temperature is above 40° subtract 0·55° for each degree above, and if below 40° C. add 0·55° for each degree below.

Valenta's Acetic-acid Test. — Reference has already been made to the use of this in the examination of butter fat (p. 134). The mixture of 2·75 grms. butter fat and 3 c.c. glacial acetic acid is warmed to 40° C., when, if the butter fat is pure, the mixture should become clear. If this is the case, the liquid is now allowed to slowly cool down with constant stirring with a thermometer until it just becomes turbid, which should take place at about 30°–40° C.

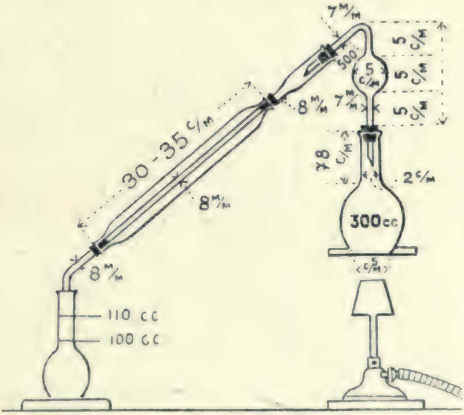


FIG. 1.

With the exception of the determination of the refractive power these methods of examination have now very largely given place to processes based on the presence of volatile fatty acids in butter, and on their differentiation from the volatile fatty acids found in coconut oil (see pp. 147 *et seq.*).

The modification of the Reichert process suggested by Wollny was, in its essential details, that adopted for the determination of butter in margarine by a Committee of the Society of Public Analysts appointed in 1900 to confer with the Principal of the Government Laboratory. The details of this process, which was formerly, until the large increase in adulteration of butter with coconut oil, or margarine containing coconut oil, the chief method for the examination of butter, are as follows (*Analyst*, 1900, 311):—

Five grams of the melted and filtered fat are weighed into a 300 c.c. flask, of the form and size shown in Fig. 1, (p. 145), and 2 c.c. of a solution prepared by dissolving 98 per cent. sodium hydroxide in an equal weight of water (care being taken to prevent absorption of atmospheric carbon dioxide), and 10 c.c. alcohol (92 per cent.) are added. The mixture is heated under a reflux condenser, connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about thirty minutes, or until the soap is dry. One hundred c.c. of hot water, which has been kept boiling for at least ten minutes, are added, and the flask heated until the soap is dissolved. Forty c.c. of $\frac{N}{1}$ sulphuric acid, and three or four fragments of pumice, or broken pipe-stem, are introduced, and the flask is at once connected with a condenser by means of a glass tube 7 mm. wide and 15 cm. from the top of the cork to the bend. At a distance of 5 cm. above the cork is a bulb 5 cm. in diameter. The flask is supported on a circular piece of asbestos 12 cm. in diameter, having a hole in the centre 5 cm. in diameter, and is first heated by a very small flame to melt the insoluble fatty acids, though the heat must not be sufficient to cause the liquid to boil. The heat is increased, and, when fusion is complete, 110 c.c. of the liquid are distilled off into a graduated flask, the distillation lasting about thirty minutes (twenty-eight to thirty-two minutes). The distillate is shaken, 100 c.c. filtered, transferred to a beaker, 0·5 c.c. of an alcoholic phenol-phthalein solution (1 per cent.) added, and the filtrate titrated with $\frac{N}{10}$ sodium hydroxide or barium hydroxide until pink. A blank experiment is carried out in precisely the same way, using the same reagents, but omitting the fat, and the amount of $\frac{N}{10}$ alkali required to neutralise this distillate should not exceed 0·3 c.c. The difference between the volumes of alkali required with the butter fat and in the blank determination, multiplied by 1·1, gives the Reichert-Meissl-Wollny value.

The improvements in the methods of refining coconut and palm-kernel oils during recent years have led to the addition of considerable quantities of those oils to edible fats, and thus has somewhat reduced the value of this process for distinguishing pure from adulterated butter, owing to the fact already mentioned, that coconut and palm-kernel oils contain a notable quantity of volatile fatty acids. A very large number of methods has been proposed for detecting coconut oil in butter, and such terms as "silver value," "caprylic-acid value," "oxygen equivalent," have appeared in the literature of the subject.

Probably the most valuable of all these tests is one devised by Polenske (*Zeit. Untersuch. Nahr. Genussm.*, 1904, vii. 273–280), which is based upon the determination of the volatile insoluble fatty acids which distil in the Reichert-Wollny process. This method, which is known as the Reichert-Wollny-Polenske process, is now very generally employed for the analysis of butter, but to obtain concordant results it must be carried out strictly under the specified conditions and in an apparatus of the form and dimensions shown in the figure (Fig. 2).

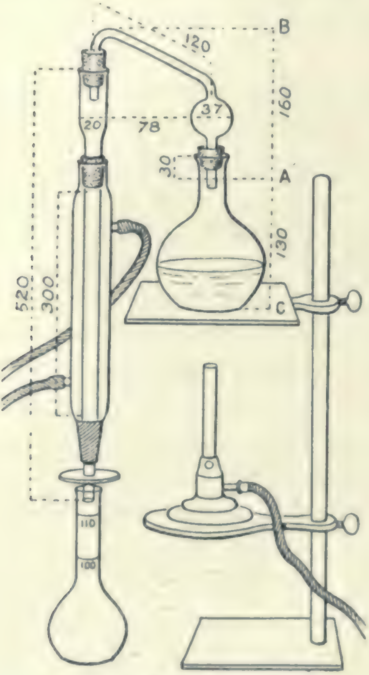


Fig. 2.

The details of the process are as follows :—

Five grams of the clear butter fat are weighed out into a 300 c.c. flask, and saponified as described on p. 146 with 20 grms. glycerin and 2 c.c. of a 50 per cent. aqueous solution of sodium hydroxide, the heating being effected with a Bunsen burner. When saponification is complete, and the mixture perfectly clear, it is allowed to cool down below 100° C., and the soap dissolved in 90 c.c. of water. To this solution, which should be clear and almost colourless, are now added 50 c.c. of dilute sulphuric acid containing 2·5 per cent. sulphuric acid, and the flask attached to the condenser. The distillation is now proceeded with as usual, the heat being so regulated that 100 c.c. of distillate pass over in nineteen to twenty minutes, and the temperature of the condensing water is between 18° and 20° C. As soon as 110 c.c. of distillate have been collected the receiver is changed, and a 25 c.c. cylinder put in its place. The receiver is now transferred (care being taken to mix its contents as little as possible) to a water-bath at a temperature of 10° C., where it is kept for ten minutes, the surface of the water being just above the 110 c.c. mark. The insoluble fatty acids rise into the neck of the flask, and, in the case of butter, are in the form of solid, opaque granules, and with pure coconut oil in the form of clear, oily drops. The latter are also obtained in the case of mixtures containing more than 10 per cent. of coconut oil. The liquid is mixed and filtered, the Reichert-Wollny value being determined on the filtrate by titration with $\frac{N}{10}$ alkali.

The condenser, cylinder, and receiver are next washed with 18 c.c. of water, the washings being passed through the filter paper, and the insoluble fatty acids remaining on the filter dissolved in alcohol. The solution obtained is titrated with $\frac{N}{10}$ barium hydroxide solution, using phenol-phthalein as indicator, the number of c.c. required being termed the " new butter value " of the fat.

This value was stated by Polenske to range, for pure butters having Reichert-Meissl values of 23·3–30·1, from 1·5–3·0, and for coconut oils having Reichert-Meissl values of 6·8–7·7, from 16·8–17·8. Mixtures with Reichert-Meissl values between 23 and 27 gave "new butter values" of from 1·6–1·9, a rise of 1·0 in the Reichert-Meissl figure corresponding with an increase of 0·1 in the "new butter value," and each per cent. of coconut oil increasing the new butter value by 0·1 above that given by a genuine butter possessing the same Reichert-Meissl value. By this method it is possible to detect the presence in butter of 10 per cent. and upwards of coconut oil.

A process similar in principle, but differing in method, has been proposed by Muentz and Coudon (*Ann. d. l'Inst. Agron.*, 1904, iii. Part I.; *Analyst*, 1905, 155). In this, 10 grms. of the fat, melted and weighed at 60° C., are placed in a cylindrical vessel, and saponified by first stirring for ten minutes with 5 c.c. of potassium hydroxide solution, containing 120 grms. potassium hydroxide in 100 c.c., and then heating to 70°–80° for twenty minutes. The saponified fat is washed into a distilling flask with 200 c.c. of water, gently warmed until solution is complete and the fatty acids liberated by adding 30 c.c. of phosphoric acid (sp. gr. 1·15), any carbon dioxide being removed by connecting the vessel with a pump for ten minutes.

The volatile fatty acids are then distilled off in the apparatus shown in Fig. 3, and to obtain comparable results, strict adherence to the form and dimensions given must be made. Two hundred c.c. are distilled, the heat being regulated so that this takes about one and a half hours, and the distillate is allowed to stand until the following day, when it is filtered through a wet paper, the flask washed with 5 c.c. of water, which is also passed through the paper, and the soluble fatty acids titrated with standardised lime-water, with phenolphthalein as indicator.

The filter is now washed with four successive quantities of 5 c.c. of alcohol, poured on drop by drop, and the washings collected in the receiver originally used. The condenser is next rinsed, first with 20 c.c. of alcohol, which should fill the tube when closed at its lower end, and a second time with 5 c.c. of alcohol, these washings being added to the remainder, and the whole titrated with the standard lime-water.

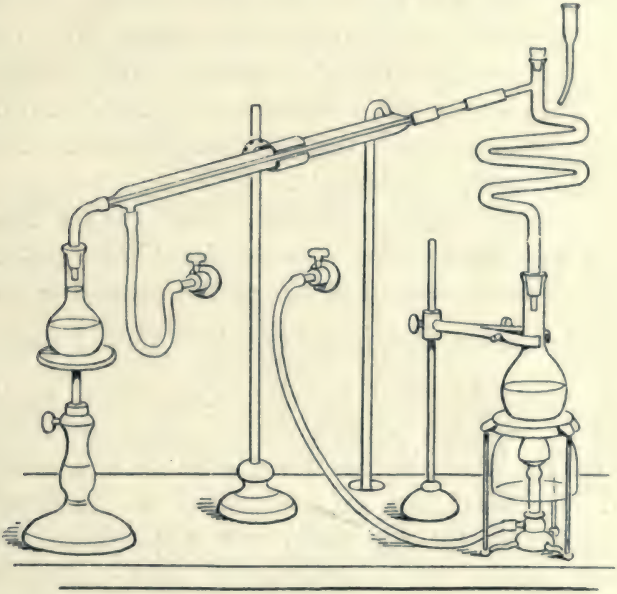


FIG. 3.

The results of both titrations are expressed as butyric acid, and the ratio $\frac{\text{insoluble acids}}{\text{soluble acids}} \times 100$ for pure butter should lie between 10 and 15, whilst for coconut oil it is 250–280. For butter containing 10 per cent. of coconut oil the figure is 19·8, and 15 per cent. coconut oil 24·1; for 20 per cent. coconut oil 27, and for 50 per cent. coconut oil 73·1. It is claimed that by this process the presence in butter of as little as 5 per cent. of coconut oil can be detected with certainty.

Two methods have been proposed, based on the precipitation of insoluble silver caprylate: (1) by Kirschner (*Zeit. Untersuch. Nahr. Genussm.*, 1905, ix. 65–70), and (2) by Wijsman and Reijst (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi. 267–271).

In the former process, 5 grms. of the fat are treated by the before-mentioned Reichert-Meissl-Wollny process so far as neutralising 100 c.c. of the filtered distillate with $\frac{N}{10}$ barium hydroxide solution. Half a gram of silver sulphate is then added to the neutral solution, which is frequently shaken for one hour, and filtered, and 100 c.c. of the filtrate are transferred to a distilling flask. To this liquid are now added 35 c.c. of dilute sulphuric acid ($2\frac{1}{2}$ per cent.) and a few fragments of pumice, and the whole distilled until 110 c.c. of distillate have been obtained. This is filtered, and 100 c.c. titrated with $\frac{N}{10}$ barium hydrate solution, the number of c.c. required, calculated back to the 5 grms., giving what is termed the "second titration value."

According to Kirschner, the percentage of butter fat in a mixture of butter and coconut oil may be calculated from the formula:—Percentage of butter fat $= 4·319\ S - 0·456\ R - 2·15$, where $S =$ the second titration value, and $R =$ the Reichert-Meissl figure. A similar formula is given for the percentage of coconut oil, which = 7·42 R − 8·116 S − 3·57. Wijsman and Reijst's method, or the "*silver value*" method, is carried out by treating with silver nitrate (1) the Reichert-Wollny distillate; and (2) 250 c.c. filtered from 300 c.c. of distillate obtained from a further 5 grms. of fat, this being saponified, treated with acid, and 100 c.c. distilled off in the usual way, after which 100 c.c. more water are added from a tap funnel, and another 100 c.c. distillate collected, this being once more repeated.

In both cases the filtered solutions are neutralised with $\frac{N}{10}$ alkali, and 40 c.c. of $\frac{N}{10}$ silver-nitrate solution added, the precipitated silver salt collected on a filter and washed until about 200 to 300 c.c. of filtrate have been collected, after which 50 c.c. of $\frac{N}{10}$ sodium-chloride solution are added and the excess of chloride titrated back with $\frac{N}{10}$ silver-nitrate solution, potassium chromate being used as indicator.

Eleven-tenths of the number of c.c. required in the first case, and six-fifths of that used in the second, give what are termed the first and second "silver values."

In the case of pure butter all the caprylic acid should distil over in the first 110 c.c., so that the "second silver value" should not exceed the first, but with coconut oil the distillation of caprylic acid continues with the second and third 100 c.c. of distillate, so that the second silver value is greater than the first. The process has been adversely criticised by Jean (*Ann. de Chim. Anal.*, 1906, ii. 121–124).

A useful qualitative test for the detection of even small quantities of coconut oil in butter is that due to Hinks (*Analyst*, 1907, 160). In this, 5 c.c. of the melted and filtered fat are dissolved in 10 c.c. of ether, and cooled to 0° C. for thirty minutes. The solidified glycerides are then rapidly filtered off, the filtrate evaporated, and the residue re-dissolved in three to four times its volume of boiling 96 to 97 per cent. alcohol. This is allowed to cool to the ordinary temperature, and then placed in a water-bath at 5° C., at which temperature it is kept for fifteen minutes. The alcoholic layer is filtered off into a tube cooled to 0° C., and the flocculent precipitate, which soon separates, is examined microscopically with a magnification of 250–300. Butter treated in this manner deposits round, granular masses, whereas coconut oil gives fine needle-shaped crystals. As little as 5 per cent. of coconut oil may be detected by this process.

Ross (*Analyst*, 1908, 457) has attempted to make this process quantitative by determining the refraction of the residues obtained, but without success.

Palm oil in butter may be detected by the Liebermann-Storch reaction for resin. Ten c.c. of the filtered fat are dissolved in 10 c.c. of acetic anhydride, and one drop of sulphuric acid (sp. gr. 1·53) added. The mixture is shaken, and, on standing, a blue liquid, having a greenish tint, separates, if palm oil is present.

Shrewsbury and Knapp (*Analyst*, 1910, xxxv. 385) have based a method of estimating coconut oil upon the fact that lauric acid, the predominating fatty acid in that fat, is readily soluble in dilute alcohol and may be determined by titrating the solution. Using a mixture of methylated alcohol of sp. gr. 0·822 with 36 c.c. of water, and titrating 70 c.c. of the alcoholic filtrate of the fatty acids with $\frac{N}{10}$ sodium hydroxide, they found that coconut oil gave a value of 163, whilst butter fat gave results ranging from 23·6 to 31·2, and a mixture of butter with 15 per cent. of coconut oil a value of 38·0 c.c.

Another method, depending upon temperature at which the barium salts show a turbidity in alcoholic solution, has been devised by Burnett and Revis (*Analyst*, 1913, xxxviii. 255). The Polenske value is determined as described above, with the difference that $\frac{N}{10}$ baryta solution is used for the titration. The insoluble barium salts are washed with 93 per cent. alcohol and dissolved in boiling alcohol (10 times the quantity of the Polenske value), the flask being heated beneath a reflux condenser. The solution is then stirred in a test-tube, and the temperature at which it becomes turbid is noted.

In the case of coconut oil a turbidity temperature of 52·5° C. was observed, with palm-kernel oil 58·5° C. Cohune-nut oil showed a similar result to that given by coconut oil.

Soluble and Insoluble Fatty Acids — the Hehner Value.—A weighed quantity of about 5 grms. of the filtered butter fat is introduced into a strong 6-oz. bottle, and 50 c.c. of approximately $\frac{N}{2}$ alcoholic potassium hydroxide solution added, another 50 c.c. being also placed in an empty flask. The bottle is fitted with an india-rubber stopper, which is secured by wire, and is placed in a water-bath, being occasionally removed, and well agitated without bringing the liquid in contact with the stopper. After about thirty minutes, saponification is complete (this being shown by the contents of the bottle being free from oily globules), and the bottle is withdrawn and allowed to cool. The stopper is then removed, and the contents of the bottle transferred, by rinsing with boiling water, into a 10-oz. flask, which is placed, together with the flask containing only alcoholic potassium hydroxide solution, on a steam-bath.

As soon as all the alcohol has evaporated the contents of each flask are neutralised with $\frac{N}{2}$ hydrochloric acid, an excess of about 1 c.c. of acid being added, and a note made of the quantity used. The flask containing the butter fat is nearly filled with boiling water, and placed on the water-bath, a cork with a long upright tube being inserted. When the fatty acids have melted to a clear liquid on the surface of the water, the flask is removed and its contents allowed to become perfectly cold, when the fatty acids should solidify. By gently tapping the sides of the flask this cake is detached, and the liquid is poured through a filter into a large flask. This liquid should have a distinct odour of butyric acid, especially on warming.

The flask containing the insoluble fatty acids is again filled with boiling water, the cork and reflux tube inserted, and the liquid gently heated to the boiling point, after which the flask is removed and thoroughly shaken until the melted fatty acids are emulsified with the water. The fatty acids are now allowed to separate again on the surface, solidified by cooling, detached by gently tapping, and the liquid filtered off as before. The process is repeated three times, or until the washings collected separately do not require more than 0·2 c.c. of $\frac{N}{10}$ sodium hydroxide solution for neutralisation.

The mixed washings are next diluted to one litre or other convenient volume, and an aliquot part titrated with $\frac{N}{10}$ sodium hydroxide solution, the number of c.c. required being calculated upon the whole liquid. This amount of alkali is that required to neutralise the excess of acid added after saponification, together with the soluble fatty acids, and the former may be known by titrating the excess in the blank experiment, so that the difference between these two titrations gives the alkali absorbed by the volatile fatty acids. These are usually expressed as butyric acid, C_3H_7COOH, the percentage of which may be found by multiplying the number of c.c. of alkali solution required to neutralise the soluble fatty acids by 0·0088 and by 100, and dividing by the weight of fat taken.

The Insoluble Fatty Acids are determined by allowing the flask containing the solid cake to drain as completely as possible, melting the fatty acids, and pouring them on to the wet filter through which the solution of soluble fatty acids was passed. They are then washed on the filter with boiling water, and the funnel filter transferred to a small beaker and placed in the water-bath until all the fatty acids have filtered through. Flask, funnel, and filter paper are well washed with ether, the washings added to the filtered fatty acids, and the ether evaporated. The fatty acids are then dried in the oven at 100° C. until constant in weight, and from the weight obtained the percentage of insoluble fatty acids is calculated on the weight of butter fat taken. This is known as the Hehner value.

Butter should contain at least 5 per cent. of soluble fatty acids calculated as butyric acid, and the insoluble fatty acids should not exceed 89·5, rarely 88·5 per cent.

The following table contains results obtained by Thorpe (*Journ. Chem. Soc.*, 1904, 254) with 357 samples of British butters :—

Number of Samples.	Reichert-Meissl-Wollny Number.	Specific Gravity at $\frac{37{\cdot}8^\circ\text{ C.}}{37{\cdot}8^\circ\text{ C.}}$	Saponification Equivalent.	Refractometer Number at 45° C.	Soluble Acids per cent. on Fat.	Insoluble Acids per cent. on Fat.	Mean Molecular Weight of Insoluble Acids.
7	22·5	0·9101	255·4	42·0	4·3	90·1	266·9
17	23·5	0·9104	253·4	41·5	4·5	89·7	265·5
15	24·5	0·9108	251·3	41·5	4·7	89·4	265·0
27	25·5	0·9110	251·1	41·3	4·8	89·3	264·2
37	26·5	0·9113	248·9	41·0	4·9	88·9	261·9
51	27·5	0·9114	247·4	40·6	5·2	88·7	261·7
78	28·8	0·9118	245·7	40·1	5·4	88·4	260·9
56	29·5	0·9120	244·0	40·1	5·6	88·3	259·6
41	30·5	0·9123	242·4	39·9	5·8	87·9	260·1
18	31·3	0·9125	241·5	39·7	5·7	87·9	258·0
10	32·6	9·9130	241·2	39·4	6·0	87·7	257·8
357							

Casein (Curd).—This may be estimated by transferring the dry butter used in determining the water to a dry filter of known weight, washing it thoroughly with ether or petroleum spirit until free from fat, and weighing the filter after drying at 100° C. The residue includes casein and salt, and the latter may be determined as described below, and subtracted from the total residue.

The amount of casein does not usually exceed 1 to 2 per cent., but cases are recorded when adulteration with casein has been practised, and as much as 5 to 6 per cent. found.

Salt.—For most practical purposes, the ash remaining after burning either the dried butter, or the residue insoluble in ether, may be taken as salt (sodium chloride).

If desired, the sodium chloride may be estimated by extracting the butter with 10 to 20 c.c. of hot water in a separating funnel, separating the aqueous layer, repeating this about ten to fifteen times, and titrating the aqueous washings with standard silver nitrate solution, using potassium chromate as indicator.

The proportion of salt may vary from 0·5 for a fresh butter up to 11 per cent. for a salt butter, but should not go beyond the latter limit (see also p. 62).

Colouring Matters.—The natural colouring matter of butter, which is termed "lactochrome," is insoluble in alcohol or glacial acetic acid, so that if on shaking the sample with either of these re-agents a coloured extract is obtained, artificial colouring matter has undoubtedly been added.

Two general schemes have been devised for the detection of artificial colouring matters in butter or margarine: (1) devised by Leeds (*Analyst*, 1887, 150), in which the fat and colouring matter are first extracted with petroleum ether, and the colouring matter dissolved out of the ethereal extract with $\frac{N}{10}$ potassium hydroxide, and reprecipitated with dilute hydrochloric acid; and (2) that devised by Cornelison (*Journ. Amer. Chem. Soc.*, 1908, 1478), who extracts the colouring matter directly by means of glacial acetic acid.

Leeds's process is carried out by mixing 100 grms. of the sample with 300 c.c. light petroleum spirit (sp. gr. 0·638), separating the ethereal layer by means of a separating funnel, and washing it with 100 c.c. of water in successive small quantities. The ethereal extract is allowed to stand for fifteen to twenty hours surrounded by ice, and is then decanted from any separated "stearin"

Colouring Matter.	Concentrated Sulphuric Acid.	Concentrated Nitric Acid.	Sulphuric Acid and Nitric Acid.	Concentrated Hydrochloric Acid.
Annatto . .	Indigo blue changing to violet.	Blue becoming colourless on standing.	Same.	No change, or only slight dirty yellow and brown.
Annatto and decolorised butter.	Blue becoming green and slowly changing to violet.	Blue through green and bleached.	Decolorised.	No change, or only slight dirty yellow.
Turmeric . .	Pure violet.	Violet.	Violet.	Violet changing to original colour on evaporation of HCl.
Turmeric and decolorised butter.	Violet to purple.	Violet to reddish violet.	Same.	Very fine violet.
Saffron . . .	Violet to cobalt-blue changing to reddish brown.	Light blue changing to light reddish brown.	Same.	Yellow changing to dirty yellow.
Saffron and decolorised butter.	Dark blue changing quickly to reddish brown.	Blue through green to brown.	Blue quickly changing to purple.	Yellow becoming dirty yellow.
Carrotin . .	Umber brown.	Decolorised.	Ditto with NO_2 fumes and odour of burnt sugar.	No change.
Carrotin and decolorised butter.	Reddish brown to purple similar to turmeric.	Yellow and decolorised.	Same.	Slightly brown.
Marigold . .	Dark olive green. Permanent.	Blue changing instantly to dirty yellow green.	Green.	Green to yellowish green.
Safflower . .	Light brown.	Partially decolorised.	Decolorised.	No change.
Aniline yellow .	Yellow.	Yellow.	Yellow.	Yellow.
Martius' yellow .	Pale yellow.	Yellow reddish precipitate, magenta at margin.	Yellow.	Yellow precipitate treated with NH_3 deflagrates.
Victoria yellow .	Partially decolorised.	Same.	Same.	Same colour returns on neutralising with NH_3.

and shaken with 50 c.c. of $\frac{N}{10}$ potassium hydroxide solution. The alkaline extract is separated, made faintly acid with dilute hydrochloric acid, and the precipitated colouring matter filtered off, together with a trace of fatty acid, which is always dissolved out by the alkali. The colouring matter may then be identified by the tests given above.

In Cornelison's method 10 grms. of the melted fat are thoroughly shaken with 10 to 20 grms. of glacial acetic acid, at about 35° C., the mixture allowed to separate, and the acid liquid drawn off. The colour of the latter is noted, and portions are treated with various re-agents to identify the colouring matter. The table on p. 162 gives the results obtained with the colouring matters mentioned, incorporated with pure butter in the proportion of 1 part in 100,000.

PRESERVATIVES (see p. 67)

Boron Compounds.—The presence of these may be detected by thoroughly mixing some of the butter with excess of water in a mortar, pouring off the water, acidifying with a drop of dilute hydrochloric acid, and moistening a piece of turmeric paper with the solution. The paper is then dried in the oven, when, if boron compounds are present, the paper develops a reddish pink tint, changing to dark blue when moistened with weak alkali.

The amount of boron compound may be readily estimated by Richmond and Harrison's modification of Thomson's process. Twenty-five grams of the sample are weighed into a 100 c.c. stoppered cylinder, and, after determination of the moisture present, sufficient water is added to bring the total volume of water up to such a quantity that 1 c.c. corresponds to 1 grm. of butter.

Dye.	Colour of Acid Extract.	Concentrated Nitric Acid.	Concentrated Sulphuric Acid.	Sulphuric Acid and Ether to Clear Solution.
(Pure natural butter)	Colourless.	Colourless.	Faint pink on standing.	Colourless.
Soudan I. (pure)	Decided pink.	Strong pink.	Strong clear pink.	Pink.
Butter yellow (impure).	Very faint pink.	Faint pink.	Faint pink.	Faint colour.
Cerasine orange G. (Casella).	Strong greenish yellow.	Acid yellow; oil - globule, salmon-pink.	As with HNO_3.	Brownish yellow.
Yellow O.B. (Haller and Merz).	Decided bright yellow.	Acid faint pink; oil-globule, salmon-pink.	As with HNO_3.	Pink.
Yellow A.B. (Heller and Merz).	Slight warm ochre-yellow.	Pink; fat colourless.	Brownish pink; oil faint pink.	Pink.
Annatto	Dull yellow.	Little change.	Faint pink on standing.	Very faint yellow.
Curcumine	Intense greenish yellow.	Dull ochre-yellow.	Strong pink.	Yellow.
Carrotin	Very faint greenish yellow.	Faint yellow.	Faint pink on standing.	Very faint yellowish.
"Alderney butter colour" (Heller and Merz).	Brownish yellow.	Strong pink.	Strong pink.	...
Ranson's butter colour ("vegetable").	Yellow.	Almost decolorised.	As with HNO_3.	...
"Dandelion brand" butter colour ("vegetable").	Yellow.	Almost decolorised.	As with HNO_3.	...

From 10 to 15 c.c. of chloroform are now introduced, and the contents of the flask heated, shaken, and allowed to separate. An aliquot portion of the aqueous liquid is then removed by means of a pipette, evaporated to dryness, ignited, and the residue extracted with hot water. The extract is made neutral to methyl orange, boiled to expel carbon dioxide, half its volume of neutral glycerin added, and the mixture titrated with $\frac{N}{10}$ sodium hydroxide solution until pink to phenol-phthalein. Each c.c. of $\frac{N}{10}$ sodium hydroxide solution is equivalent to 0·0062 grms. of boric acid.

Another method, devised by Richmond and Harrison (*Analyst*, 1902, 181), is to weigh out 25 grms. of the sample in a beaker, add 25 c.c. of a solution containing 6 grms. of milk sugar and 4 c.c. of $\frac{N}{1}$ sulphuric acid, in 100 c.c. of water. The beaker is placed in a water-oven until the fat has just melted, and the contents are then stirred well, allowed to separate, and 20 c.c. of the aqueous liquor withdrawn. A few drops of phenol-phthalein are added, and the liquid heated to the boiling point, and titrated with $\frac{N}{2}$ sodium hydroxide solution until faintly pink, after which 12 c.c. of glycerin are added, and more $\frac{N}{2}$ sodium hydroxide solution run in until a faint pink colour is again obtained. The amount of alkali required in the second titration, less the alkali required to neutralise 12 c.c. of the glycerin, multiplied by 0·0368, gives the amount of boric acid in 20 c.c. of the aqueous extract, and the percentage may be calculated by multiplying by (100 + percentage of water in the butter), and dividing by 20. In an average butter the number of c.c. of $\frac{N}{2}$ sodium hydroxide solution used, multiplied by 0·2, approximates closely to the percentage of boric acid.

The best method of testing for benzoic acid, salicylic acid, fluorides, and β-naphthol is to extract the melted butter with a dilute solution of sodium bicarbonate, and to examine this extract for the various preservatives.

Thus, in testing for benzoic and salicylic acids, the alkaline extract is exactly neutralised with dilute hydrochloric acid, and a solution of ferric chloride added. If benzoic acid or a benzoate has been added, a buff-coloured precipitate will be immediately thrown down, and if salicylic acid has been employed, an intense violet coloration will be produced.

Numerous methods have been suggested for detecting even very minute admixtures of benzoic acid or benzoates, among which may be mentioned those of Halphen (*Journ. Pharm. Chim.*, 1908, 201) and Robin (*Ann. de Chim. Anal. Appl.*, 1908, 431).

Halphen's test depends on the conversion of the benzoic acid into ammonium diamino-benzoate, which, in alkaline solution, has a brown-red colour. A quantity of the butter is melted with sufficient lime-water to render the aqueous liquor which separates distinctly alkaline. After cooling, the latter is separated, acidified with phosphoric acid, and extracted with ether. The ether is allowed to evaporate spontaneously, and the residue dried at the ordinary temperature, after which it is gently heated with 2 c.c. of concentrated sulphuric acid until completely dissolved. An addition of 0·2 c.c. of fuming nitric acid is now made, and the solution transferred to a dry test-tube and heated carefully over a small flame until sulphuric-acid fumes appear. After cooling, the mixture is diluted with 5 or 6 c.c. of water, which causes nitrous fumes to be evolved. When again cold, a saturated solution of sodium sulphite is added drop by drop until all yellow vapours have disappeared. Ammonia is then allowed to flow over the surface of the solution, and if benzoic acid is present, an orange-red coloration is produced, the intensity of which is proportional to the quantity of benzoic acid. In case no coloration is produced, the absence of benzoic acid may be confirmed by adding a drop of ammonium sulphide to the ammoniacal solution, when, if benzoic acid is present, a red coloration develops at the point of contact of the two liquids.

By Robin's process it is claimed that as little as twelve parts per 100,000 of sodium benzoate may be detected with certainty. The test is carried out by shaking 25 grms. of the melted butter with a solution of 0·4 to 0·5 grm. of sodium bicarbonate in 50 c.c. of water, and 15 c.c. of 95 per cent. alcohol, and allowing the mixture to stand for ten minutes, after which the alcoholic layer is drawn off, acidified with 7 or 8 drops of hydrochloric acid, and heated to the boiling point. It is then shaken with a little talc, and filtered, the cold filtrate extracted in a separating funnel with 40 c.c. of ether, and the ethereal extract washed once with a mixture of 20 c.c. of water, 5 c.c. of 95 per cent. alcohol, and 0·2 to 0·3 grm. of sodium bicarbonate. The alkaline alcoholic extract is evaporated on the water-bath, and the residue carefully warmed with a mixture of 5 c.c. of concentrated sulphuric acid and 10 drops of fuming nitric acid, until white fumes appear, after which the liquid is poured into 50 c.c. of water containing a small piece of turmeric paper. A yellow coloration indicates the presence of benzoic acid, which may be confirmed by adding ammonia solution until alkaline, then a few drops of ammonium sulphide solution, and shaking the vessel. In the presence of benzoic acid the colour changes from yellow to reddish orange.

Fluorides.—The presence of these may be detected in the absence of boric acid by evaporating a small quantity of the alkaline extract to dryness in a platinum crucible, igniting the residue, moistening it with a few drops of concentrated sulphuric acid, and covering the mouth of the crucible with a piece of glass, coated with paraffin wax, through which some marks have been scratched.

Fluorides may also be detected by applying the above process to the aqueous liquid, which separates when a sample of the butter is melted.

If boric acid is present, the fluoride is liable to be lost by volatilisation as boron fluoride. It is necessary, therefore, to separate the borate as calcium borate, by rendering the liquid alkaline with lime-water, evaporating it to dryness, and extracting the residue with dilute acetic acid, which dissolves calcium borate. The insoluble matter is then dried, and treated with concentrated sulphuric acid as described above.

MARGARINE, VEGETABLE BUTTER, OR OTHER BUTTER SUBSTITUTES

The analysis of these is a matter requiring a considerable amount of skill, and even when the analysis is made, very long experience is necessary before a right interpretation can be put upon the chemical and physical data obtained.

The only requirements for margarine under the Sale of Food and Drugs Act, 1899, are that the sample shall not contain more than 16 per cent. water or more than

10 per cent. of butter. The same restrictions as to preservatives apply to this as to genuine butter.

The amount of water is readily determined by the method given under "Butter" (p. 144). The method officially adopted by the Committee of the Society of Public Analysts for the estimation of butter is the Reichert-Meissl-Wollny process (p. 146), the maximum permissible limit for the Reichert-Wollny value being 4, and a Reichert-Wollny value of 7·1 being regarded as indicative of the presence of 20 per cent. butter fat.

In addition to the analysis of margarine to ensure compliance with these standards, it is often desirable to endeavour to determine the precise composition of a sample of artificial butter, such as the relative proportions of animal and vegetable fats, and the particular fats or oils of which they consist. It is here where only prolonged experience can decide what tests to apply and determine the correct interpretation to put upon the results obtained.

In an exhaustive analysis, the specific gravity, saponification value, iodine value, titre, and Reichert-Wollny-Polenske figures should always be determined, and such qualitative tests as Halphen's for cotton-seed, Baudouin's for sesamé oil, the arachidic acid test for arachis oil, and the Liebermann-Storch test for palm oil applied.

The tests for colouring matters and preservatives are the same as for natural butter.

LARD

In addition to the tests mentioned in Chapter VI, pp. 84 *et seq.*, Halphen's test for cotton-seed oil and Baudouin's test for sesamé oil should be applied, and, if thought desirable, arachis oil may be tested for by the arachidic acid method. The presence of as little as 2 to 3 per cent. cotton-seed oil may be detected by the phytosteryl acetate test (see p. 132), and the addition of maize oil, which is sometimes used for adulterating lard, will also be shown by the same method.

Preservatives may be detected, and, if present, estimated as described under "Butter."

CHEESE

The composition of cheese is so variable that it is to be regretted there are no standards to which it should conform.

The proportion of fat may vary from 20 per cent. or less to 35 or 40 per cent., or, in a cream cheese, up to 75 per cent., whilst the water may be anything between 20 and 40 per cent.

The analysis of cheese should include determinations of the proportions of water, ash, fat, and nitrogen, and an examination of the fatty matter.

Water.—This may be determined by drying a weighed quantity of about 5 grms. of the sample, cut in thin slices, in the oven at 105° C., until constant in weight.

Ash.—The dried cheese, as obtained in the above determination, is ignited at as low a temperature as possible, and the residue weighed when the whole of the carbon has been burned away.

Fat.—This may be determined approximately by grinding up 25 to 50 grms. of the dried cheese with ignited sand, and extracting the mixture in a Soxhlet apparatus with ether or petroleum spirit, the extract being collected in a weighed carbonic-acid flask, from which the solvent is afterwards distilled off, and the residue dried in the oven at 105° C. and weighed.

A better method is that of Palmquist, which is a modification of the Rose-Gottlieb process. In this, about 1 grm. of the cheese is weighed into a Gottlieb tube, 10 c.c. of 2·5 per cent. ammonia solution added, and the mixture warmed on the water-bath, and shaken until a milky homogeneous solution is obtained. After cooling, 10 c.c. alcohol and 25 c.c of ether are added, the tube being thoroughly shaken after each addition. An addition of 25 c.c. of petroleum spirit is then made, and the tube, after being again well shaken and inverted, is allowed to stand for a few hours for its contents to separate, after which the ethereal layer is siphoned into a weighed flask. A second extraction of the mass remaining in the tube is then carried out in an exactly similar manner, the ethereal extract being again siphoned into the weighed flask, the solvent distilled off, and the residue dried in the oven at 105° C., and weighed.

A larger quantity of the fat for its examination may be readily prepared by cutting up a quantity of the cheese, wrapping it in a piece of muslin, and suspending it over a basin in an oven at 105° C. The clear fat collected should then be examined, and its Reichert-Wollny value, which should be similar to that of butter, determined. If the Reichert-Meissl-Wollny figure is abnormal, the fat requires further systematic examination by the processes mentioned under " Margarine " (p. 167), to detect foreign fats.

Nitrogen.—This is estimated by heating 1 to 2 grms. of the cheese with concentrated sulphuric acid and a globule of mercury, as in the well-known Kjeldahl process. The proteins may be calculated by multiplying the percentage of nitrogen by 6·3.

CHOCOLATE

No standards have yet been legally fixed in this country for any of the various forms of chocolate, though such standards are in existence on the Continent, and are urgently needed in view of the large amount of adulteration practised in this industry. Not only is the natural fat of the chocolate replaced by other fats, such as coconut oil, and coconut stearine, or palm-nut stearine, and the chocolate adulterated with excessive husk or starch, but products are sold as milk or cream chocolate which have no right to such designations. Hence N. P. Booth presented to the International Congress of Applied Chemistry, held in London in 1912, the following proposed standards, which are not more stringent than those adopted by some continental countries and by some of the Colonies :—

1. *Unsweetened Chocolate* must be prepared exclusively from roasted, shelled, finely ground cocoa-beans, with or without the addition of a small quantity of flavouring matter. It should contain not less than 45 per cent. of cacao butter.

2. *Sweetened Chocolate.*—A preparation consisting exclusively of the products of roasted, shelled, finely ground cocoa-beans, and not more than 65 per cent. of sugar, with or without a small quantity of harmless flavouring matter.

3. *Granulated or Ground Chocolate for Drinking Purposes.*—The same definition as for sweetened chocolate should apply here, except that the proportion of sugar may be raised to not more than 75 per cent.

4. *Chocolate-covered Goods.*—Various forms of con-

fectionery covered with chocolate, the composition of the latter agreeing with the definition of a sweetened chocolate.

5. *Milk Chocolate.*—A preparation composed exclusively of roasted, shelled cocoa-beans, sugar, and not less than 15 per cent. of the dry solids of full-cream milk, with or without a small quantity of harmless flavouring matter.

The analysis of chocolate should comprise determinations of the moisture, ash, fat, fibre, total nitrogen, and sugar, and an examination of the nature of the fatty matter and sugar.

In the case of milk chocolate, or cream chocolate, the fatty matter should contain both cacao butter and butter fat, and the sugar should contain lactose.

The analysis is carried out as follows :—

Water.—A weighed quantity of about 5 grms. is finely divided, and dried in the oven at 105° C., until constant in weight.

Ash.—The dried product obtained in the determination of the moisture is cautiously burnt until all carbonaceous matter is volatilised. The proportion of ash should not exceed 1 to 1·5 per cent., unless the sample has been coloured with mineral colouring matter, such as ochre.

Fat.—This may be estimated by extracting 5 grms. of the finely ground sample in an extraction thimble with ether or light petroleum spirit, by means of a Soxhlet apparatus. The extracting liquid is collected in a small weighed flask, which, when extraction is complete, is detached from the Soxhlet apparatus, the solvent distilled off, and the residual fat weighed, after being dried in the oven at 105° C.

Kreutz (*Zeit. Untersuch. Nahr. Genussm.*, 1908, 584–586) recommends melting the sample with chloral alcoholate prior to extraction with ether. From 2 to 3 grms. of the chocolate are placed in a small flask with 3 to 4 grms. of chloral alcoholate, and the mixture melted by heating on a water-bath. The hot mass is well stirred with 10 to 15 c.c. of ether, a further 35 c.c. of ether added, and, after thorough shaking, the mixture is filtered through a dry filter. The filtrate is passed through the filter again and again until perfectly bright, and the residue on the filter washed three times with ether. The ether is then distilled off, and any chloral alcoholate removed by heating the residue to about 75° C., under reduced pressure. The residue obtained is extracted with carbon tetrachloride and filtered to eliminate a little theobromine and colouring matter, the filtrate evaporated in a weighed flask, and the residue of fat dried in the oven at 105° C. and weighed.

For the examination of the fat a larger quantity may be prepared by simply shaking up about 15 to 20 grms. of the finely ground sample in a stoppered bottle with three or four successive quantities of petroleum spirit, allowing the mass to settle, pouring off the solvent, and evaporating it. The residual fat should then be examined for its refractive power, its Reichert-Meissl-Polenske values, its saponification value, its iodine value, and its titre.

Genuine cacao butter gives a refractometer reading at 35° C. of about 49°, has a Reichert-Meissl value of 1 or rather less, a saponification value of about 286 to 290, an iodine value of about 34, and a titre of about 48° C. Coconut oil has a refractive power of only about 37°, and is thus readily detected by this, as also by the much increased saponification value and reduced iodine value, and the increased Reichert-Meissl figure.

Coconut stearine also increases the saponification value, reduces the iodine value, and raises the Reichert-Meissl figure. Palm-nut stearine increases the saponification value, reduces the iodine number, and slightly raises the Reichert-Meissl figure, its own Reichert-Meissl value being about 2·2.

Of the other fats said to be used as substitutes for cacao butter, and mentioned in Chapter VIII, p. 117:—

Dika, or Gaboon Fat, raises the saponification value, lowers the iodine value, but does not affect the Reichert-Meissl figure.

Borneo Tallow, or Tankawang Fat, has analytical values very similar to those of cacao butter.

Illipé Fat has a much higher iodine value (54 to 68). (See also p. 117.)

Fibre.—This is best estimated by Allen's method (*Commercial Organic Analysis,* iii., Part II., p. 567), in which 2 grms. are freed from fat, and boiled for thirty minutes under a reflux condenser with 200 c.c. of water and 2½ c.c. of sulphuric acid. The liquid is filtered through linen, and the residue thoroughly washed with hot water and boiled with 200 c.c. of 1¼ per cent. solution of sodium hydroxide. The residue is filtered off, washed with hot water, alcohol, and ether, and dried at 110° C. and weighed. It is then ignited, and the loss regarded as crude fibre.

Total Nitrogen.—This is estimated on about 2 grms. of chocolate by the Kjeldahl method. In an ordinary chocolate it is normally about 1 per cent., and in a milk chocolate slightly higher. In a plain chocolate the proportion of nitrogen, multiplied by 20, will give the percentage of fat-free cocoa.

Sugar.—This may be determined in plain chocolate by means of a polarimeter, a 20 per cent. aqueous solution, which is clarified with lead acetate in the ordinary way, being used. In the case of milk chocolate the introduction of lactose complicates the determination slightly, but estimation of the copper-reducing power enables the lactose to be calculated, and an allowance made for its effect on the optical rotation.

CHAPTER X

STATISTICS OF THE TRADE IN EDIBLE OILS

In basing any conclusions as to the consumption of edible oils upon the figures published by the Customs authorities of different countries, allowance must be made for the fact that in many cases (*e. g.* seed oils) it is not possible to distinguish the quantities used for food from those used for soap and lubricating purposes.

United Kingdom Trade.—The following figures are taken from the tables published annually by the Board of Trade, and show the import of oils during the ten years ending 1908:—

Oils.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.	1908.
Coconut . cwts.	458,297	552,743	478,143	495,860	782,632	615,238	613,165	335,545	335,781	555,335
Olive . . tuns	15,939	12,044	15,488	18,978	14,485	15,101	7,690[1]	9,419[1]	7,391[1]	6,330[1]
Palm . . cwts.	945,472	938,350	1,212,111	1,446,298	1,234,004	1,309,176	1,144,368	1,223,787	1,508,023	1,317,995
Seed oils . tuns	46,416	41,131	48,842	35,454	36,001	10,553	3,309[1]	1,786[1]	1,111[1]	2,203[1]

[1] Not including refined oil.

The amounts of the chief edible oils and their value imported into this country during the three years ending 1909 were as follows :—

Imports

Oil.	1907.	1908.	1909.	1907.	1908.	1909.
Crude :—				£	£	£
Coconut . . . cwts.	357,815	555,335	502,408	634,357	757,812	752,257
Olive . . . . tuns	7,391	6,330	4,788	287,254	243,497	241,905
Palm . . . . cwts.	1,508,923	1,317,995	1,762,641	1,896,133	1,559,266	2,195,620
Refined :—						
Coconut . . . cwts.	118,903	203,077	177,085	223,522	323,334	315,690
Cotton-seed . . tuns	14,226	15,251	17,560	365,512	401,506	242,139
Olive . . . tuns	4,937	5,822	4,186	...	...	...
Palm . . . . cwts.	18,656	35,838	58,645	251,634	293,308	276,743
Butter . . . cwts.	4,210,156	4,210,821	4,062,833	22,417,926	24,080,912	22,425,067
Margarine . . cwts.	885,068	813,447	868,292	2,223,645	2,081,245	2,243,737
Lard from U.S.A. cwts.	1,903,961	1,924,881	1,703,578	4,491,539	4,407,410	4,857,199
Lard from other countries . . cwts.	61,170	62,610	56,707			
Imitation lard . cwts.	222,090	174,064	231,847	408,192	306,700	438,909

Exports

Oil, etc.	1907.	1908.	1909.	1907.	1908.	1909.
Crude :—				£	£	£
Coconut . cwts.	56,058	56,887	61,247	95,074	79,563	89,327
Olive . . tuns	...	26	70	...	1,341	3,915
Palm . . cwts.	4,946	415	1,787	7,568	543	2,554
Refined :—	...	...	...	846,037	705,020	822,923
Butter . cwts.	12,305	10,045	9,214	68,591	59,324	54,825
Lard . . cwts.	9,634	8,118	5,506	26,340	22,340	18,722
Imitation lard cwts.	568	583	792	1,000	1,008	1,604

In the case of the crude oils mentioned in the above tables it is probable that the bulk was used for technical purposes.

It is interesting to note the effect of the War upon the imports and exports of edible oils and oil-seeds as shown by the figures for the years from 1913 to 1919 :—

NUTS AND KERNELS FOR EXPRESSING OIL

Imports from all Sources

	1913.	1914.	1915.	1916.	1917.	1918.	1919.
Copra . tons	30,868	66,494	48,540	62,400	52,400	7,930	71,531
Arachis nuts	—	—	—	—	137,578	135,768	107,108
Palm-kernels	—	74,797	233,249	248,501	248,160	295,334	304,423
Other sorts .	50,250	27,566	96,448	69,121	9,218	4,379	16,791

OILS

Imports

	1913.	1914.	1915.	1916.	1917.	1918.	1919.
Fish oils, etc. . . tons	70,886	52,537	91,872	108,867	52,726	64,421	54,775
Animal oils . . . cwts.	224,324	192,134	191,029	51,776	27,353	57,278	178,777
Coconut (unrefined) cwts.	546,742	309,417	323,332	154,943	27,665	8,792	473,099
Olive (refined) . . tuns	6,163	6,388	6,213	5,180	2,179	2,970	4,030
Cotton-seed oil (refined . . . . tons	16,586	19,866	33,771	10,098	8,537	17,264	25,541
Soya-bean oil . . tons	—	—	—	—	3,502	596	29,683
Other seed oils (excepting linseed and rape oils) . tons	20,380	24,314	42,168	48,471	9,771	2,471	7,432
Oleomargarine and refined tallow . cwts.	377,557	363,676	645,767	650,584	626,405	1,488,099	1,009,744

Exports

	1913.	1914.	1915.	1916.	1917.	1918.	1919.
Refined Coconut . cwts.	58,913	56,260	100,599	39,293	10,435	17	8,812
Palm and palm-kernel	15,168	20,153	47,858	30,232	—	—	—
Palm-kernel . . cwts.	—	—	—	—	94,851	26,290	2,658
Cotton-seed . . . tons	25,013	27,062	21,505	2,407	632	51	2,708
Soya-bean . . tons	9,390	9,321	13,473	4,554	608	—	1,039
Other seed oils	2,287	3,160	3,060	1,620	7,176	5,004	1,642
Oleomargarine and animal fat . . cwts.	258,508	181,191	155,120	74,639	14,579	2,489	21,582

According to statistics published by Slaus-Kantschlieder (*Chem. Rev. Fett Ind.*, 1909, xvi. 223–231), the importations into Nice amounted to 8,264,900 kilos in 1907, as compared with 11,917,200 kilos in 1906.

The quantities of olive oil exported from Nice to various countries during the two years were as follows :—

Exported to—	1906.	1907.
	Kilos.	Kilos.
Austria-Hungary	351,000	370,000
Germany	748,000	749,000
Russia	436,000	624,000
England	234,000	206,000
Switzerland	313,000	289,000
Roumania	70,000	123,000
Servia	14,000	21,000
Bulgaria	4,000	5,200

Italian Trade in Olive Oil.—The Italian Customs authorities give the following details of the exports of refined and other grades of olive oil during the three years ending 1907, the quantities being in quintals (one quintal equals 220·46 lbs.) :—

Refined Olive Oil

Exported to—	1907.	1906.	1905.
	Quintals.	Quintals.	Quintals.
United States	29,188	71,400	38,687
Austria-Hungary	28,998	22,203	7,752
Germany	15,690	11,132	5,490
Great Britain	5,861	9,432	4,102
Holland	12,648	73,519	8,403
Switzerland	7,626	11,294	6,936
Egypt	15,353	19,285	4,867
Other Countries	8,536	8,894	4,900
Totals	123,900	227,159	81,137
Total Values	$1,471,122	$2,051,652	$945,600

Other Grades of Olive Oil

Exported to—	1907.	1906.	1905.
	Quintals.	Quintals.	Quintals.
Austria-Hungary	19,013	25,834	18,293
France	60,766	116,312	43,191
Germany	17,793	21,222	11,058
Great Britain	25,000	29,739	22,184
Russia	26,677	22,854	29,765
Switzerland	7,124	8,819	5,668
Egypt	2,636	5,810	1,956
United States	82,198	95,258	52,577
Brazil	14,495	12,320	8,820
Argentina	90,347	109,194	58,256
Uruguay	9,402	8,190	3,893
Other Countries	32,976	33,032	17,440
Totals	388,427	488,584	273,101
Total Values	$9,370,801	$11,787,041	$6,852,104
Grand Totals	512,327	715,743	354,238
Grand Total Values	$10,861,923	$13,838,693	$7,797,704

Spanish Oil Trade.—Some interesting details of the production of olive oil in Spain were given in the *Board of Trade Journal* for September 1907. The average output of the oil was estimated at 200,000 metric tons. In 1906 it amounted to 133,665 tons (metric), as against 149,249 tons in 1905. The deficiency in the crop of 1906 accounted for the falling-off of the exports of oil in that year, though owing to the official pecuniary encouragement given to the manufacture of seed oils in Spain, there was not a corresponding increase in the importations of oils employed as substitutes for olive oil.

The imports of seed oils, coconut and palm-nut oils and oil seeds into Spain, and the exports of olive oil during the years 1905 and 1906 and the first six months of 1907, were as follows :—

Spanish Oil Trade

	1905.	1906.	First six months of 1907.
Imports :—	Metric tons.	Metric tons.	Metric tons.
Seed oil	684	895	330
Coconut and palm-nut oil .	279	548	400
Oil seeds	39,526	45,233	32,917
Export :—			
Olive oil	34,228	18,911	6,150

The further development of the olive-oil trade in Spain is illustrated by the following figures from the *Board of Trade Journal* for June 1917 :—

	Olives.	Olive Oil.
	Metric tons.	Metric tons.
1914	1,181,431	207,765
1915	1,772,887	326,108
1916	1,146,599	207,115

Vegetable Oil Trade in France.—The following details of the trade of France in vegetable oils are given by the *Oil, Paint, and Drug Rep.*, April 4, 1910 :—

During 1909, 141,080 metric tons of copra (coconut pulp) were imported into France as against 169,357 tons in 1908, and 110,008 tons in 1907, nearly the whole of the quantity going to Marseilles.

About 40 per cent. of the imports were from the Philippines, 29 per cent. from the Dutch Indies, 9 per cent. from British India, 8 per cent. from Mauritius, and the remainder from other countries.

The total values of oil products used in France in 1909 were officially estimated at £2,044,500, including: Arachis nuts, £4,511,000; linseed, £1,999,800; sesamé seed, £892,000; mustard and Indian rape seed, £864,000; poppy seed, £399,800; and cotton seed (chiefly Egyptian), £262,000.

The following figures show the imports of oil seeds into Marseilles during the three years:—

	1907.	1908.	1909.
	Tons.	Tons.	Tons.
Sesamé	68,836	41,749	64,087
Arachis nuts, shelled	113,219	85,653	170,012
Arachis nuts, unshelled	123,304	102,188	155,056
Linseed	21,202	17,085	16,962
Rape and ravison	5,082	2,202	5,795
Poppy seed	4,106	2,334	2,356
Castor seed	16,370	18,111	11,553
Pulghere	520	709	1,818
Cotton seed	15,884	14,497	14,249
Niger and kapok	6,351	3,701	5,118
Copra	109,744	163,999	136,655
Palm kernels	4,412	1,675	3,639
Mowrah, illipé, etc	12,781	11,146	8,856
Totals	501,811	465,049	596,156

The only oils imported in any quantities were cotton-seed, olive, and palm oils, the average importations of which during the last five years were:—

	Tons.
Cotton-seed oil	24,000
Olive oil	22,000
Palm oil	16,000

The copra imported is chiefly used in the manufacture of soap, though about a third is manufactured into edible coconut oil and vegetable butters.

The coconut oil exported from Marseilles (chiefly to England, the United States, Switzerland, and Austria) amounted to 23,840 tons in 1909, whilst 22,726 tons were sent from Marseilles to other parts of France.

Oil-seed Trade in India.—The trade in arachis nuts was greatly affected by the War, the exports being reduced by about 50 per cent. This was mainly owing to the shortage of transport and high freights, but especially to the suspension of the demand from Marseilles. In 1913 about 80 per cent. of the total exports of arachis nuts from India went to France.

The cotton-seed trade being mainly with the United Kingdom was much less affected than the exports of sesamé or arachis seeds.

The following figures given by the *Board of Trade Journal* for 1916, show the exports of oil seeds from India in 1914 and 1915:—

	1913–1914.	1914–1915.
	Tons.	Tons.
Copra	3,800	32,000
Cotton seed	281,000	208,000
Arachis nuts	278,000	138,000
Sesamé seed	112,000	47,000

Cotton-seed Oil in the United States.—The growth of the now gigantic cotton-seed oil industry in the United States is illustrated by the following figures given by the *Oil, Paint, and Drug Rep.*, June 7, 1909, which show the production and exports of the seed and its product since 1872:—

Production of Cotton Seed and Oil

Year ending June 30.	Cotton Seed.		Oil Produced.	Cake and Meal Produced.
	Produced.	Manufactured.		
	Tons.	Tons.	Gallons.	Tons.
1909 . . .	5,903,838	3,669,747	146,789,880	1,491,752
1908 . . .	4,952,402	2,564,873	103,049,820	1,043,080
1907 . . .	5,912,646	3,843,981	153,759,240	1,785,804
1906 . . .	5,060,205	3,131,175	125,700,928	1,271,740
1904 . . .	4,716,591	3,241,426	121,877,618	1,155,568
1902 . . .	4,630,311	3,154,417	118,606,079	1,124,550
1900 . . .	4,668,346	2,479,386	93,325,729	884,391
1890 . . .	3,494,811	873,702	34,948,000	305,800
1880 . . .	2,615,608	235,404	9,416,000	82,400
1875 . . .	1,686,516	84,325	3,373,000	29,500
1872 . . .	1,317,637	52,705	2,108,000	18,400

Exports

Year ending June 30.[1]	Cotton Seed.		Oil.		Cake and Meal.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
	Tons.	$	Gallons.	$	Tons.	$
1909	...	...	...	...	...	...
1908	14,239	353,213	41,029,991	17,226,451	464,644	11,889,415
1907	8,814	209,493	41,880,304	17,074,403	670,484	17,062,594
1906	11,859	268,330	43,793,519	13,673,370	555,417	13,073,100
1904	6,430	141,174	29,013,743	10,717,280	410,175	9,134,088
1902	28,202	509,627	33,042,848	12,992,393	525,233	12,271,009
1900	24,928	346,230	46,902,390	14,127,538	571,852	11,229,188
1890	3,830	74,575	13,384,385	5,219,178	...[2]	...
1880	6,071	134,116	6,997,796	3,225,414	...	...
1875	2,658	63,128	417,387	216,640	...	...
1872	3,180	72,212	547,165	293,546	...	...

[1] The figures in this table relate to the seed crop of the previous year.

[2] Not separately shown.

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